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ANNUAL REPORTS

ON THE

PROGRESS OF CHEMISTRY.

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ANNUAL REPORTS

ON THE

PROGRESS OF CHEMISTRY

FOR 1917.

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TABLE OF ABBREVIATIONS EMPLOYED IN THE REFERENCES.

Abbreviated Title.	Journal.
A.	Abstracts in Journal of the Chemical Society.*
Abh. Böhm. Akad.	Abhandlungen der Böhmischen Akademie.
Acad. Sci. Fennicae	Acta Societatis Scientiarum Fennicae.
Ally. Brau. Hopfen. Zeit.	Allgemeine Brau- und Hopfen-Zeitung.
Amer. Chem. J.	American Chemical Journal.
Amer. J. Sci.	American Journal of Science.
Anal. Fis. Quim.	Anales de la Sociedad Española Fisica y Quimica.
Anal Soc. Quim. Argentina	Anales de la Sociedad Química Argentina.
Analyst	The Analyst.
Annalen	Justus Liebig's Annalen der Chemie.
Ann. Bot.	Annals of Botany.
Ann. Chim.	Annales de Chimie.
Ann. Chim. anal.	Annales de Chimie analytique appliquée à l'Industrie, à l'Agriculture, à la Pharmacie et à la Biologie.
Ann. Chim. Applicata	Annali di Chimica Applicata.
Ann. Chim. Phys.	Annales de Chimie et de Physique.
Ann. des Mines	Annales des Mines.
Ann. Inst. Pasteur	Annales de l'Institut Pasteur.
Ann Physik	Annalen der Physik.
Ann. Report	Annual Reports of the Chemical Society.
Ann. Sci. Agron.	Annales des Sciences Agronomiques.
Arb. Deut. Landw. Ges.	Arbeiten der Deutschen Landswirtschaftlichen Gesellschaft.
Arch. Farm. sperim.	Archivio di Farmacologia sperimentale e Scienze affini.
Arch. Pharm.	Archiv der Pharmazie.
Arkiv. Kem. Min. Geol.	Arkiv för Kemi, Mineralogi och Geologi.
Astrophys. J.	Astrophysical Journal.
Atti R. Accad. Lincei	Atti della Reale Accademia dei Lincei.
Ber.	Berichte der Deutschen chemischen Gesellschaft
Ber. Deut. bot. Ges.	Berichte der Deutschen botanischen Gesellschaft.
Ber. Deut. pharm. Ges.	Berichte der Deutschen pharmazeutischen Gesellschaft.
Ber. Deut. physikal. Ges.	Berichte der Deutschen physikalischen Gesellschaft.
Ber. K. Sächs. Ges. Wiss.	Berichte über die Verhandlungen der Königlich Sächsischen Gesellschaft der Wissenschaften.
Bied. Zentr.	Biedermann's Zentralblatt für Agrikulturchemie und rationellen Landwirtschafts-Betrieb.
Biochem. J.	The Biochemical Journal.
Biochem. Zeitsch.	Biochemische Zeitschrift.
Boll. chim. farm	Bolletino chimico farmaceutico.
Bot. Gaz.	Botanical Gazette.
Brit. Pat.	British Patent.
Bull. Acad. Sci. Petrograd	Bulletin de l'Académie Impériale des Sciences de Petrograd.
Bull. Agric. Intell., Rome	Bulletin of the Bureau of Agricultural Intelligence and of Plant Diseases, Rome.

* The year is not inserted in references to 1917

Abbreviated Title.	Journal.
Bull. Amer. Inst. Min. Eng.	Bulletin of the American Institute of Mining Engineers.
Bull. Assoc. Chim. Sucr. Dist.	Bulletin de l'Association des Chimistes de Sucrerie et de Distillerie.
Bull. Sci. Pharmacol.	Bulletin des Sciences Pharmacologiques.
Bull. Soc. chim.	Bulletin de la Société chimique de France.
Bull. Soc. franç Min.	Bulletin de la Société française de Minéralogie.
Centr. Bakt. Par.	Centralblatt für Bakteriologie, Parasitenkunde und Infektionskrankheiten.
Centr. Min.	Centralblatt für Mineralogie, Geologie und Palæontologie.
Chem. Weekblad	Chemisch Weekblad.
Chem. Zeit.	Chemiker Zeitung.
Chem. Zentr.	Chemisches Zentralblatt.
Compt. rend.	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
Deut. Landw. Presse	Deutsche Landwirtschaftliche Presse.
Eng. and Min. J.	Engineering and Mining Journal.
Fr. Pat.	French Patent.
Fühlings Landw. Zeit.	Fühlings Landwirtschaftliche Zeitung.
Gazzetta	Gazzetta chimica italiana
Illustr. Landw. Zeit.	Illustrirte Landwirtschaftliche Zeitung.
Int. Mit. Bodenkunde.	Internationale Mitteilungen für Bodenkunde.
Inter. Zeitsch. Phys.-chem. Biol.	Internationale Zeitschrift für physikalisch-chemische Biologie.
Jahrb. Min. Beil. Bd.	Neues Jahrbuch für Mineralogie, Geologie und Palæontologie, Beilage-Band.
Jahrb. Radioaktiv. Elektronik	Jahrbuch der Radioaktivität und Elektronik.
J. Agric. Research	Journal of Agricultural Research.
J. Agric. Sci.	Journal of Agricultural Science.
J. Amer. Chem. Soc.	Journal of the American Chemical Society.
J. Biol. Chem.	Journal of Biological Chemistry, New York.
J. Bd. Agric.	Journal of the Board of Agriculture.
J. Chem. Met. and Min. Soc. S. Africa	Journal of the Chemical, Metallurgical and Mineralogical Society of South Africa.
J. Chim. phys.	Journal de Chimie physique.
J. Geol.	Journal of Geology.
J. Hygiene	Journal of Hygiene.
J. Ind. Eng. Chem.	Journal of Industrial and Engineering Chemistry.
J. Landw.	Journal für Landwirtschaft.
J. Path. Bact.	Journal of Pathology and Bacteriology.
J. Pharm. Chim.	Journal de Pharmacie et de Chimie.
J. Physical Chem.	Journal of Physical Chemistry.
J. Physiol.	Journal of Physiology.
J. pr. Chem.	Journal für praktische Chemie.
J. Roy. Agric. Soc.	Journal of the Royal Agricultural Society.
J. Russ. Phys. Chem. Soc.	Journal of the Physical and Chemical Society of Russia.
J. Soc. Chem. Ind.	Journal of the Society of Chemical Industry.
J. Washington Acad. Sci.	Journal of the Washington Academy of Sciences.
Journ. Chem. Soc.	Journal of the Chemical Society.
Koll. Chem. Beihefte	Kolloidchemische Beihefte.
Kolloid Zeitsch.	Kolloid-Zeitschrift.
Lancet	The Lancet.
Landw. Versuchs-Stat.	Die landwirtschaftlichen Versuchs-Stationen.
Medd. Nobel Inst.	Meddelanden från Kongl. Vetenskapsakademiens Nobel-Institut.
Mem. Coll. Sci. Kyōtō	Memoirs of the College of Science, Kyōtō Imperial University.

Abbreviated Title.	Journal.
Mem. Manchester Phil. Soc.	Memoirs and Proceedings of the Manchester Literary and Philosophical Society.
Met. Chem. Eng.	Metallurgical and Chemical Engineering.
Min. Mag.	Mineralogical Magazine and Journal of the Mineralogical Society.
Mitt. deut. Landw. Ges.	Mittheilungen der deutschen Landwirtschaftlichen Gesellschaft.
Monatsh.	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften.
Münch. Med. Woch.	Münchener Medizinische Wochenschrift.
Nachr. Ges. Wiss. Göttingen	Nachrichten von der Königlichen Gesellschaft der Wissenschaften zu Göttingen.
Naturwiss. Rundschau	Naturwissenschaftlich Rundschau.
Oesterreich. Zeitsch. Zuckerind.	Oesterreichische Zeitschrift für Zuckerindustrie.
P.	Proceedings of the Chemical Society.
Pharm. Weekblad	Pharmaceutisch Weekblad.
Philippine J. Sci.	Philippine Journal of Science.
Phil. Mag.	Philosophical Magazine (The London, Edinburgh and Dublin).
Phil. Trans.	Philosophical Transactions of the Royal Society of London.
Proc. K. Akad. Wetensch. Amsterdam.	Koninklijke Akademie van Wetenschappen te Amsterdam. Proceedings (English version).
Proc. Physiol. Soc.	Proceedings of the Physiological Society.
Proc. Roy. Irish Acad.	Proceedings of the Royal Irish Academy.
Proc. Roy. Soc.	Proceedings of the Royal Society.
Proc. Roy. Soc. Edin.	Proceedings of the Royal Society of Edinburgh.
Proc. Soc. Exp. Biol. Med.	Proceedings of the Society for Experimental Biology and Medicine.
Quart. J exp. Physiol.	Quarterly Journal of Experimental Physiology.
Rec. trav. chim.	Recueil des travaux chimiques des Pays-Bas et de la Belgique.
Riv. Min. Crist. Ital.	Rivista di Mineralogia e Cristallografia Italiana.
Schweiz. Apoth. Zeit.	Schweizerische Apotheker Zeitung.
Skand. Archiv Physiol.	Skandinavisches Archiv für Physiologie.
Soil Sci.	Soil Science.
T.	Transactions of the Chemical Society.
Trans. Faraday Soc.	Transactions of the Faraday Society.
U.S. Pat.	United States Patent.
Wien. klin. Woch.	Wiener klinische Wochenschrift.
Wien. Landw. Zeit.	Wiener Landwirtschaftliche Zeitung.
Zeitsch. anal. Chem.	Zeitschrift für analytische Chemie.
Zeitsch. angew. Chem.	Zeitschrift für angewandte Chemie.
Zeitsch. anorg. Chem.	Zeitschrift für anorganische und allgemeine Chemie.
Zeitsch. Elektrochem.	Zeitschrift für Elektrochemie.
Zeitsch. Hygiene	Zeitschrift für Hygiene und Infektionskrankheiten.
Zeitsch. Kryst. Min.	Zeitschrift für Krystallographie und Mineralogie.
Zeitsch. Nahr.-Genussm.	Zeitschrift für Untersuchung der Nahrungs- und Genusmittel.
Zeitsch. physikal. Chem.	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.
Zeitsch. physiol. Chem.	Hoppe-Seyler's Zeitschrift für physiologische Chemie.

ANNUAL REPORTS

ON THE

PROGRESS OF CHEMISTRY.

GENERAL AND PHYSICAL CHEMISTRY.

The continuance of war conditions has led to a further diminution in the volume of published research, and until comparatively late in the year it seemed to the writer doubtful whether the record of progress would warrant the publication of a full Report. To a very considerable extent, the pages of German journals dealing with physical chemistry and physics have served to record the work of investigators belonging to neutral countries, the contributions made by Germans being relatively very small in comparison with normal times. The *Zeitschrift für physikalische Chemie*, the first issue of which marked the beginning of a new era in the development of physical chemistry, has now ceased to appear, the reason advanced for its suspension being that suitable paper can no longer be obtained.

Atomic Weights.

The sources of error involved in the accurate determination of combining ratios have been discussed in a series of papers[1] published during the past two years. In the last of these publications[2] it is of interest to find that much of the recent work on combining ratios affords confirmation of the view, first expressed by G. D. Hinrichs,[3] that the combining ratio is a function of the quantity of substance employed in the determination. The explanation of this anomaly, which was put forward by Hinrichs, is not, however, accepted by the authors, who point out that the anomaly

[1] Compare *Ann. Report*, 1916, 36.

[2] P. A. Guye and E. Moles, *J. Chim. phys.*, 1917, **15**, 360, 405.

[3] *Compt. rend.* 1893, **115**, 1074; *A*, 1893, ii, 163; *ibid.*, 1893, **116**, 753; *A*, 1893, ii, 316; *ibid.*, 1894, **118**, 528; *A.*, 1894, ii, 276.

is only to be found in the results of series of determinations, in which the substances have been weighed in air in the usual way, reduction to a vacuum being effected by calculation. This suggests that the apparent variation of the combining ratio with the quantity of substance is due to the condensation of air, water, etc., on the surface of the solid substances, and in support of this explanation it is found that the various types of curves, which express the relation between the combining ratio and the quantity of substance operated on, can all be accounted for on the assumption that condensation films give rise to errors in weighing.

Isotopes.

Although the view that isotopes cannot be separated from one another by chemical means has met with fairly general acceptance, this question has been submitted to further investigation.[4] The nitrate obtained from carnotite lead, containing one part of ordinary lead, three parts of radium-*G*, and a trace of radium-*B*, was submitted to fractional crystallisation more than a thousand times. A determination of the atomic weight of the metal in the least and most soluble fractions gave numbers agreeing within 0·006 per cent., which is well within the limits of the possible experimental error. The β-ray activity of the two fractions was also found to be identical within the limits of the experimental error of 1 per cent. From these observations it is inferred that the molecular solubilities of the nitrates of the isotopes are identical, and further evidence is thus obtained in support of the view that isotopes cannot be separated by crystallisation processes.

According to Soddy,[5] the question of the separability of isotopes is not to be judged by any one particular line of evidence, whether this consist in the proof that each radio-element has an isotope to which it is more closely allied than to any of the other elements, or of experiments in which a given pair of isotopes has been submitted to the same operation a very large number of times or to different operations corresponding with possible modes of separation, but by the agreement of the results given by all three methods of inquiry.

If the molecular solubilities of the salts of isotopic elements are identical, then, since the molecular weights are different, it follows that the solubilities, expressed in grams per litre, and the densities of the saturated solutions ought to show slight differences. Measurement[6] of the densities of saturated solutions of the nitrates pre-

[4] T. W. Richards and N. F. Hall, *J. Amer. Chem. Soc.*, 1917, **39**, 531; *A.*, ii, 230.

[5] F. Soddy, *ibid.*, 1614; *A.*, ii, 437.

[6] K. Fajans and J. Fischler, *Zeitsch. anorg. Chem.*, 1916, **95**, 284; *A.*, ii, 472.

pared from ordinary lead of atomic weight 207·15, and from carnotite lead with an atomic weight of 206·59, has shown that there is an appreciable difference, the density of ordinary lead nitrate solution being the greater. Assuming that the molecular volumes of the isotopes are identical, and that the change of volume in the formation of the saturated solutions is the same for both, it would seem that the difference in the densities of saturated solutions of salts of isotopic elements may be utilised for the determination of the relative atomic weights of the isotopes. The difference between the densities should bear the same ratio to the mean density as the difference of the atomic weights to the mean atomic weight. Experiments made [7] with the nitrates of ordinary, carnotite, and pitchblende lead have, indeed, given results which appear to justify the application of the method.

The view that the *X*-ray spectra of isotopes are identical finds confirmation in the observation [8] that the wave-lengths of the lines in the *L* series and also of the α and β lines in the *M* series of lead and radium-*G* agree to within $0{\cdot}0001 \times 10^{-8}$ cm.

Atomic Structure.

Our knowledge of atomic structure has made but little progress during the year under review. A further interesting contribution [9] has, however, been made by W. D. Harkins to his series of papers [10] on the evolution of the elements and on the nature of the periodicity which is conditioned by the evolutionary process.

The assumption that the elements are derived from hydrogen by a process, in which the formation of helium nuclei represents a primary and distinct stage in the process of agglomeration, leads to the view that the elements should fall into two series, one of these beginning with helium and containing elements of even atomic number, the other beginning with lithium and containing elements of odd atomic number. Two such series are actually distinguishable in the group of radio-elements, and further evidence of this dual periodicity is afforded by the numbers which express the relative abundance of the different elements. Whether the relative abundance in the earth's crust, in meteorites, or in the lithosphere is considered, it appears that the even-numbered elements occur in much greater quantity. If the elements are plotted in the order of their atomic numbers, the even-numbered elements are in all cases much

[7] K. Fajans and M. Lembert, *Zeitsch. anorg. Chem.*, 1916, **95**, 297 *A.*, ii, 472.

[8] M. Siegbahn and W. Stenström, *Compt. rend.*, 1917, **165**, 428 ; *A.*, ii, 524.

[9] W. D. Harkins, *J. Amer. Chem. Soc.*, 1917, **39**, 856 ; *A.*, ii, 303.

[10] Compare *Ann. Report*, 1916, 2, 253, 254.

more abundant than the adjacent odd-numbered elements. Furthermore, if the elements are arranged in the order of their abundance, the first seven elements are all even-numbered.

It is natural to suppose that the abundance will bear some relation to the stability of the atomic nucleus, and that the stability will depend on the structure of the nucleus. Hence the above facts seem to favour the idea of a dual periodicity as predicted by the hydrogen–helium structural hypothesis. Such periodicity is, of course, independent of the periodicity which characterises the ordinary periodic table, and this is at once intelligible when it is remembered that the physical and chemical properties of the elements are for the most part determined by the number of the external electrons, which is not affected by the internal structure of the nucleus.

According to N. F. Hall,[11] the number of known isotopes in a pleiad and the character of the predominant radiation also show a periodic variation which is in accord with the hypothesis that the heavier atoms represent conglomerations of hydrogen and helium nuclei. The isotopes of even-numbered elements are more numerous than those of odd-numbered elements, and the former show a tendency to emit α- rather than β-rays on disintegration.

On theoretical grounds it is probable that there is some connexion between the atomic number N and the atomic frequency ν. According to H. S. Allen,[12] this relation can be expressed in the form $N\nu = n\nu_A$, in which n is an integer and ν_A a fundamental frequency, characteristic of, and common to all atoms. The same formula is also said to represent the relation between the atomic number and the frequency, which, according to the quantum theory, corresponds with the energy required to liberate an electron from the atom,[13] the only difference being that the fundamental electronic frequency ν_E has the value $3{\cdot}29 \times 10^{15}$ ($\sec^{-1}$), whereas the fundamental atomic frequency ν_A is equal to $21{\cdot}3 \times 10^{12}$ ($\sec^{-1}$).

The ionisation potential of helium, calculated on the basis of Bohr's theory, is 29·3 volts, whereas experiment has given an appreciably lower value. As a result of a redetermination,[14] in which various possible sources of error have been avoided, it seems now to be definitely established that the ionising potential is in the neighbourhood of, and not greater than, 20 volts. In view of the considerable discrepancy, it would seem that the mechanism of the ionisation process is different from that which has been previously assumed.

[11] N. F. Hall, *J. Amer. Chem. Soc.*, 1917, **39**, 1616; *A.*, ii, 438.
[12] *Phil. Mag.*, 1917, [vi], **34**, 478.
[13] *Ibid.*, 488.
[14] C. B. Bazzoni, *ibid.*, 1916, [vi], **32**, 566; *A.*, ii, 63.

According to Debye,[15] the frequencies of the K series of lines in the high frequency spectra of elements between sodium (atomic number 11) and neodymium (atomic number 60) exhibit relations which suggest that the atoms of all these elements have three electrons in the innermost ring. The elements of low atomic number have, however, a different constitution.

Emission Spectra.

The question of the nature of the Balmer series of hydrogen lines has not hitherto received a definite answer. It has been suggested by Sommerfeld that it is due to the superposition of diffuse, sharp, and principal series, but recent measurements[16] of the separation of the pairs of lines which constitute H_α and H_β afford no support for this view. On the other hand, the observed wave-length differences are quite consistent with the hypothesis that the lines in question are principal series lines.

By a method essentially the same as that previously used in the determination of the distribution of intensity in broadened spectral lines,[17] the same authors have investigated the relative intensities of hydrogen and helium lines when the spectra are produced under different conditions. The results show clearly that the relative intensities of the lines in a particular series depend on the conditions of the electrical discharge, and that under conditions in which there is a transfer of energy from the longer to the shorter wave-lengths in a given series there is a concomitant transference of energy from one series to another, in the sense that the associated series, and more particularly the diffuse series, are relatively enhanced at the expense of the principal series. Such changes in the distribution of the line intensities are of particular interest in their bearing on the spectra of celestial bodies, and it has been found that the distribution which is characteristic of some of these stellar radiators can be approximately reproduced under laboratory conditions.

The discovery of a method which permits of observations being made in the ultra-violet region beyond the limit reached by Schumann and by Lyman must be ranked as a highly important development in the investigation of emission spectra. By this method it has been possible to determine[18] the most rapid vibrations which are

[15] P. Debye, *Physikal. Zeitsch.*, 1917, **18**, 276; *A.*, ii, 434.

[16] T. R. Merton and J. W. Nicholson, *Phil. Trans.*, 1917, [A], **217**, 237; *A.*, ii, 433.

[17] *Phil. Trans.*, 1916, [A], **216**, 459; *A.*, 1916, ii, 461.

[18] O. W. Richardson and C. B. Bazzoni, *Phil. Mag.*, 1917, [vi], **34**, 285; *A.*, ii, 521.

emitted by helium, hydrogen, and mercury. Although the limits of the spectra could not be fixed with any great degree of accuracy, the results indicate that the limiting frequencies are in approximate agreement with those calculated from the ionisation potentials based on Bohr's theory, and not with the potentials found in the experiments of Franck and Hertz.

Crystal Structure and the Molecular Hypothesis.

The interference effects observed when crystalline substances are examined by means of *X*-rays according to the methods of W. H. and W. L. Bragg have led to views on the structure of crystals which, to some chemists, appear to be incompatible with the ordinary molecular hypothesis as applied to solid substances. It is natural that conclusions which would seem to involve the idea that molecules have no real existence in one of the three states of aggregation should have attracted the attention of the chemist, and, in point of fact, the matter has been the subject of much discussion.

It is not merely a question of the individuality of molecules in the crystalline state, but questions of valency, of chemical affinity, of intra-molecular as distinguished from inter-molecular forces, are obviously involved.

If we except the evidence afforded by partition phenomena in the formation of solid solutions, there is, it is true, no method which permits of the determination of molecular weights in the solid state. In this respect our knowledge of solids stands on quite a different plane from that of gases and possibly of liquids, in that the Avogadro hypothesis is generally accepted as affording a general method for the determination of molecular magnitudes in the gaseous state and also in dilute solutions. Even when this difference is recognised, and it is admitted that there is no clear evidence of any continuity in the transition from the fluid to the crystalline state in any circumstances, yet many chemists will hesitate to accept the view that this transition involves such an apparently fundamental change as the obliteration of the molecule, unless the evidence in its favour is of the strongest possible kind. For the present, the evidence consists in the structural relations which seem to follow from the rational interpretation of *X*-ray interference effects, and one of the interesting problems of the future will be to reconcile the *X*-ray crystal models with the molecular hypothesis. It is, of course, not by any means universally admitted that there is any real discrepancy, but the majority of chemists undoubtedly incline towards this view.

The *X*-ray crystal models are criticised by A. Smits and F. E. C.

Scheffer,[19] who contend that the models ought to differentiate between those atoms which are chemically combined in the same molecule and those which are constituents of different molecules, although it is admitted that the distances between the molecules are smaller than the molecular diameter and that the distances between atoms which belong to different molecules are not much greater than those between atoms in the same molecule. The models are also said to conflict with the idea that chemical attraction is localised in centres, the number of which is determined by the valency of the atom.

Similar views are expressed by A. Fock,[20] J. Beckenkamp,[21] and J. Stark.[22] From considerations based on electro-affinity, the last-named considers it impossible for intra-molecular linkings to be destroyed in the crystalline state. Structural models in which the individuality of the molecules is retained are put forward by the above-mentioned authors, and it is claimed that these are equally consistent with the *X*-ray interference effects which are shown by the substances in the crystalline condition.

According to I. Langmuir,[23] the compound substances for which atomic models have been set up are not to be considered as typical, for they are all polar compounds in which the atoms are linked together by residual valencies. In such compounds, it must be supposed that the entire crystal represents a single molecule.

F. Rinne[24] maintains that the purely atomic conception of crystal structure is untenable, and contends that structural groups of atoms are clearly discernible in certain cases, although the number of molecules contained within the unit space-lattice bears no relation to the real molecular complexity of the substance. A similar view is put forward by P. Pfeiffer,[25] who, in applying the theory of valency and the rules of co-ordination to various substances which have been examined by the *X*-ray method, derives molecular formulæ for various substances in the crystalline state. In this connexion, it is pointed out that, at the present time, diamond is the only crystalline substance for which the *X*-ray structure is in agreement with the accepted valency of the constituent atoms.

[19] *Proc. K. Akad. Wetensch. Amsterdam*, 1916, **19**, 432; *A.*, ii, 78.
[20] *Centr. Min.*, 1916, 392; *A.*, ii, 129.
[21] *Ibid.*, 1917, 97; *A.*, ii, 296.
[22] *Jahrb. Radioaktiv. Elektronik*, 1915, **12**, 280.
[23] *J. Amer. Chem. Soc.*, 1916, **38**, 2221; *A.*, ii, 19.
[24] *Zeitsch. anorg. Chem.*, 1916, **96**, 317; *A.*, ii, 18.
[25] *Ibid.*, 1915, **92**, 376; *A.*, 1916, ii, 228; *ibid.*, 1916, **97**, 161; *A.*, ii, 78.

The results obtained by L. Vegard [26] in the investigation of the closely related members of the tetragonal group comprising zircon, rutile, cassiterite, xenotime, and anatase also suggest that molecular groupings are discernible in the crystal structure. The structures assigned to zircon, rutile, cassiterite, and xenotime correspond with the molecular formulæ ZrO_2,SiO_2, $(TiO_2)_2$, $(SnO_2)_2$, and YO_2,PO_2 respectively. These formulæ appear to involve the assumption that change of state may involve a change in structure, for it cannot be denied that the representation of xenotime as a phosphate of the formula YPO_4 is supported by evidence of considerable weight.

The application of *X*-ray methods of analysis to mixed crystals would seem to indicate that the interpenetration of the components is of a very intimate kind. Observations made by Bragg's method on mixed crystals containing potassium chloride and bromide, and on crystals containing potassium and ammonium bromides,[27] show that the reflection maxima from the cube and dodecahedron faces are of normal type and intermediate in position compared with the maxima exhibited by the pure components. If the crystals were built up of superimposed layers of the two components, it might be expected that the reflection spectra would show double maxima. Such double maxima are not actually found, and the conclusion is drawn that the mixed crystals have a space-lattice which is similar to that of either component, the atoms of the isomorphous elements being mutually replaceable.

This view does not accord with conclusions which have been drawn from observations [28] of a different type on mixed crystals containing zinc and magnesium sulphates, $Zn(Mg)SO_4,7H_2O$. These mixed crystals are said to differ from crystals of the component substances in the appearance of certain vicinal faces and in the mode of dehydration. In explanation of these differences, it is suggested that the mixed crystals consist of superimposed layers of the components. It is very probable, however, that the *X*-ray observations represent the indications of a much more delicate instrument, and on that account afford more trustworthy information relative to the constitution of mixed crystals.

In this connexion, reference may be made to results obtained in the examination of crystals of ammonium sulphate and rubidium sulphate. According to Tutton's crystallographic measurements,

[26] *Phil. Mag.*, 1916, [vi], **32**, 65; *A.*, 1916, ii, 405; 1916, [vi], **32**, 505; *A.*, 1916, ii, 593; 1917, [vi], **33**, 395; *A.*, ii, 296.

[27] L. Vegard and H. Schjelderup, *Physikal. Zeitsch.*, 1917, **18**, 93; *A.*, ii, 243.

[28] C. Viola, *Atti R. Accad. Lincei*, 1916, [v], **25**, ii, 285; *A.*, ii, 79.

the structural dimensions of corresponding ammonium and rubidium salts show a very close approximation to equality, and this is fully borne out by the *X*-ray investigation of the sulphates.[29] The structural relations exhibited by these salts are obviously incompatible[30] with the valency volume theory of Pope and Barlow, for this would make the volume of ammonium sulphate twice as large as that of rubidium sulphate, whereas the actual volumes of the space units are very nearly equal.

An important development in the methods used in the investigation of crystal structures is to be recorded. The methods of Bragg and von Laue demand a knowledge of the crystallographic system to which the substances under investigation belong, and also require that well-formed crystals shall be available. In the application of the new method,[31] the morphological information can be dispensed with, and the structure can be determined on crystals of microscopic or submicroscopic dimensions. The interference figures are obtained by pressing the crystalline powder to form a small rod, which is placed in the axis of a cylindrically arranged sensitive film, and subjected to the influence of monochromatic *X*-rays, when characteristic curves are obtained on the developed film, these being the result of interference phenomena conditioned by the structure of the minute crystals.

The method has been applied in the investigation of the structure of graphite and amorphous carbon, with the result that graphite is found to be trigonal and that amorphous carbon is identical in structure with graphite, the difference between the two forms consisting simply in the degree of subdivision of the substance. It would therefore seem that there are but two structurally different modifications of carbon, namely, diamond and graphite. In the former, the carbon valencies are arranged tetrahedrally, whilst in graphite three of the valencies (principal) are in one plane and inclined to one another at 120°, the fourth (secondary) valency being disposed at right angles to this plane. It is claimed that this structural difference is in harmony with the differences in the chemical properties of the two modifications.

The further investigation of secondary-ray interference figures would seem to offer a means of elucidating the relations between other so-called allotropic forms.[32]

[29] A. Ogg and F. L. Hopwood, *Phil. Mag.*, 1916, [vi], **32**, 518; *A.*, 1916, ii, 594.

[30] A. E. H. Tutton, *Proc. Roy. Soc.*, 1917, [A], **93**, 72; *A.*, ii, 244.

[31] P. Debye and P. Scherrer, *Physikal. Zeitsch*, 1917, **18**, 291; *A.*, ii, 437.

[32] J. Olie, jun., and A. J. Byl, *Proc. K. Akad. Wetensch. Amsterdam*, 1917, **19**, 920, *A.*, ii, 286.

The importance of a knowledge of crystal structure for the identification of substances is admirably demonstrated[33] in a short account of the application of the crystallographic methods of Fedorov in the identification of a minute crystal of intestinal origin, which was found to consist of phenyl salicylate.

Structure of Inorganic Compounds.

The old conception of duplex affinity, which was the foundation of the dualistic system, has recently been made use of in an attempt[34] to devise structural formulæ for complex inorganic compounds. In addition to the distinction previously made[35] between positive and negative affinity, the formulæ in question involve a further distinction between primary and secondary affinity. This secondary affinity only shows itself when the primary affinity has come into play. Compounds formed by the saturation of primary affinity only are characterised by a transfer of electrons from one atom to another, and these compounds are of the "strong electrolyte" type. "Molecular compounds" are formed by the saturation of negative affinity only, whilst saturation of both primary and secondary affinity leads to the formation of compounds of the "organic compound" or "paraffin" type. Apart from this distinction between different groups of substances, the theory offers a plausible explanation of many facts connected with the strengths of acids and bases, of the relative stabilities of metal ammonia compounds, and of the phenomenon of polymerisation.

Electrical Conductivity of Solutions.

The general adoption of the Kohlrausch method for the determination of the electrical conductivity of solutions has been facilitated by the fact that fairly accurate results can be obtained with simple apparatus of a readily accessible kind. For many purposes, this degree of accuracy is amply sufficient, but according to recent investigations, it is evident that measurements of the conductivity of solutions can be made with an accuracy far exceeding that which is usually attained. These researches[36] cover the investigation of the influence of all the various factors which affect the measurement of conductivity, including the action of the mechanism for producing alternating currents, the arrangement of the bridge

[33] T. V. Barker, *Lancet*, May 26th, 1917.
[34] S. H. C. Briggs, *T.*, 1917, **111**, 253; *A.*, ii, 254.
[35] *T.*, 1908, **93**, 1564.
[36] W. A. Taylor and S. F. Acree, *J. Amer. Chem. Soc.*, 1916, **38**, 2396, 2403, 2415; *A.*, ii, 7, 8. E. W. Washburn, *ibid.*, 1916, **38**, 2431; *A.*, ii, 10.

system, the design and construction of conductivity cells, and the sensitiveness of indicating instruments.

It has been found that the Vreeland oscillator is the best and most convenient form of instrument for the production of alternating currents for conductivity work, this form of generator giving a nearly pure sine wave which can be adjusted at will. A properly constructed telephone receiver, tuned to the frequency employed, is found[37] to be the most suitable indicating instrument, the degree of precision in the setting being limited and finally controlled only by the temperature fluctuations of the thermostat. The conductivity cell should be designed to fit the telephone, and theoretical considerations afford information which may be advantageously utilised in the construction of such cells.

Ionic Dissociation.

By general consent, the original expression for the degree of ionisation of an electrolyte has been modified by the introduction of a correction factor which, in its simplest form, involves the assumption that the ionic mobility varies inversely as the viscosity of the solution. The degree of ionisation is accordingly given by $\gamma = \lambda_v \eta_v / \lambda_\infty \eta_0$, in which η_v is the viscosity of the solution at dilution v, and η_0 is the viscosity of the pure solvent.

The values of γ for solutions of hydrochloric acid have been recently compared[38] with the corresponding values of α derived from the equation $E_2 - E_1 = 2RT \log \alpha_1 c_1 / \alpha_2 c_2$, in which E_1 and E_2 are the values of the *E.M.F.* of a cell of the type hydrogen electrode | HCl || Hg_2Cl_2 | Hg, when the concentrations of the acid are respectively c_1 and c_2. By assuming that γ and α have the same value in the most dilute solution, it is possible to compare the corresponding values in more concentrated solutions. The results are shown in the following table:

Mols. HCl per 1000 grams H_2O	0·00167	0·002	0·005	0·01	0·02	0·05	0·1	0·2	0·5	1·0
γ... ...	0·988	0·988	0·981	0·972	0·962	0·944	0·925	0·909	0·890	0·845
α... ...	0·988	0·987	0·971	0·947	0·918	0·874	0·843	0·818	0·793	0·857

It is evident that α decreases more rapidly than γ with increasing concentration, and that there is a very appreciable difference in 0·1*N*-solutions. Similar differences have been found[39] in the comparison of the γ and α values for solutions of potassium chloride.

[37] E. W. Washburn and K. Parker, *J. Amer. Chem. Soc.*, 1917, **39**, 235; *A.*, ii, 235.

[38] J. H. Ellis, *ibid.*, 1916, **38**, 737; *A.*, 1916, ii, 369.

[39] D. A. MacInnes and K. Parker, *ibid.*, 1915, **37**, 1445; *A.*, 1915, ii, 510.

In comparing thus the values of γ and α, it should be recognised that these are not identical from the theoretical point of view, for $c\gamma$ measures the ion concentration, whereas $c\alpha$ affords a measure of the chemical activity of the ion in the thermodynamic sense. By assuming that the conductivity-viscosity ratio gives the correct degree of ionisation, it is possible to calculate the value of the activity-coefficient α from freezing-point data. Such data of the requisite degree of accuracy are available in the case of solutions of potassium chloride, and the values of α calculated in this way are found to be in good agreement with the values obtained from the *E.M.F.* measurements previously referred to. It would seem legitimate to conclude from this concordance that the conductivity-viscosity ratio affords an accurate measure of the degree of ionisation, but that this is not a measure of the ion activity. In accepting this result, it should in all probability be stipulated that the true transport numbers for the electrolyte in question should be independent of the concentration of the solution.

In an attempt to find a general expression for the relation between the concentration and the degree of ionisation, which should be applicable to all electrolyte solutions, Kraus and Bray[40] put forward the formula $(c\alpha)^2/c(1-\alpha) = K + k(c\alpha)^n$, in which K, k, and n are constants determined by the nature of the electrolyte and the nature of the solvent. The same formula was independently suggested by MacDougall[41] to account for the behaviour of aqueous solutions of strong electrolytes. Somewhat later, the equation $(c\alpha)^2/c(1-\alpha) = K + k\{c(1-\alpha)\}^n$ was put forward by Szyszkowski,[42] and this author has more recently pointed out[43] that this formula is equivalent to that of Kraus and Bray, the only difference being that the deviations from the law of mass action are attributed in the one case to the influence of the ions (K. and B.) and in the other to the influence of the non-ionised molecules (S.). The fact that the ionisation reaches a minimum value at a certain concentration is perhaps more readily interpreted in terms of Szyszkowski's formula.

It has been shown that the concentration, which corresponds with this minimum ionisation, decreases as the specific inductive capacity of the solvent falls, and that for solvents of low dielectric capacity, this concentration falls within the range of solutions which are unsaturated and may be actually realised. The behaviour of

[40] *J. Amer. Chem. Soc.*, 1913, **35**, 1315; *A.*, 1913, ii, 914; *Science*, 1912, **35**, 433.

[41] *Ibid.*, 1912, **34**, 855; *A.*, 1912, ii, 826.

[42] *Medd. Nobel Inst.*, 1915, **3**, No. 2; *A.*, 1915, ii, 616.

[43] *Ibid.*, 1916, **3**, No. 11; *A.*, ii, 127.

electrolytes in such solvents has been frequently examined [44] in recent years, and it seems to be clearly established that the phenomena of ionisation in liquid media of this type differ very considerably from those which are exhibited by typical aqueous solutions. In particular, it has been shown that electrolytes in solvents of low dielectric capacity exert an ionising influence on one another, with the result that the electrical conductivity of mixtures of electrolytes in these solvents cannot be calculated by the ordinary mixture rule or by the application of the principle of isohydry.

The facts brought to light by the study of the influence of the solvent on the ionisation of electrolytes appear to shed some illumination on the question of the ionisation of salts in the fused and crystalline states.[45] There is evidence to show that the degree of ionisation of fused electrolytes varies but slightly with the temperature, the change in the electrical conductivity being almost entirely due to changes in viscosity.[46] The solidification of a fused salt is accompanied by a very large fall in the conductivity, but according to potential measurements made on a cell of the type silver | crystallised silver nitrate || fused silver nitrate | silver at the temperature of fusion of silver nitrate, it seems that there is no appreciable difference in the concentration of the silver ions in the fused and crystalline salts. From this, it follows that the fall in conductivity on solidification is to be attributed to a very large diminution in the mobility of the ions and not to a change in the degree of ionisation.

The commonly accepted view, that salts are not ionised until they are dissolved in suitable solvents, is obviously incompatible with the above hypothesis, for this assumes that normal electrolytes are appreciably ionised in the crystalline state. Substances, such as hydrogen chloride, which are non-conductors in the pure liquid condition, and yet give highly conducting solutions when dissolved in water, are regarded as anomalous, and it is supposed that these react in some way with the ionising solvent, this reaction being attended by marked thermal and other effects which accompany the dissolution process.

[44] Compare A. N. Sachanov and J. S. Prsheborovski, *Zeitsch. Elektrochem.*, 1914, **20**, 39; *A.*, 1914, ii, 92; A. N. Sachanov, *Zeitsch. physikal. Chem.*, 1914, **87**, 441; *A.*, 1914, ii, 419; A. N. Sachanov and J. S. Prsheborovski, *J. Russ. Phys. Chem. Soc.*, 1915, **47**, 849; *A.*, 1915, ii, 729; A. N. Sachanov and A. I. Rabinovitsch, *ibid.*, 1915, **47**, 859; *A.*, 1915, ii, 730.

[45] A. N. Sachanov, *J. Russ. Phys. Chem. Soc.*, 1916, **48**, 341; *A.*, ii, 115.

[46] Compare R. Lorenz, "Elektrolyse geschmolzener Salze," III, 289.

Overvoltage.

In spite of the practical importance of overvoltage effects in electrolytic reduction and oxidation processes, the phenomenon has not received any great amount of attention. With the object of supplying data which may be utilised in the production and maintenance of definite overvoltages in such electrolytic processes, systematic experiments have recently been made by E. Newbery which not only afford the requisite information for the actual practice of electrolysis, but serve to throw further light on the nature of overvoltage effects.

Results obtained with different metals in acid and alkaline solutions show that anodic overvoltages[47] are in general much higher than the corresponding cathodic effects.[48] It is mainly on this account that electrolytic reduction processes can be more easily graded, whilst electrolytic oxidation tends to give highly oxidised products, and ultimately carbon dioxide.

Although a certain ambiguity attaches to the choice of what is to be regarded as the normal value of the overvoltage, the results show fairly clearly that the magnitude of the cathodic overvoltage is determined by the position of the metal in the periodic table.[49] The metals can, in fact, be divded into nine groups, of which the last eight correspond with groups I—VIII of the periodic system. The same metal may show overvoltages corresponding with more than one group, but when this occurs, it is found, in nearly all cases, that the metal in question forms compounds in which its valency agrees with that of the other members of each of these groups. The first or zero group contains metals which, under certain conditions, show no overvoltage, but all the zero group metals are to be met with in one or more of the other groups. The overvoltage increases in equal steps in passing from group O to group II, and thereafter decreases gradually from group II to group VIII.

The existence of this relation between cathodic overvoltage and the valency of the cathode metal cannot be satisfactorily explained in terms of the older theories of Nernst, Le Blanc, and Foerster, which attribute the effects to the operation of physical, that is to say, non-chemical, forces. The theory advanced by Newbery[50] to account for the facts is distinguished from the older theories, in that it assumes that chemical forces come into play which lead to

[47] *T.*, 1916, **109**, 1066; *A.*, ii, 598. [48] *Ibid.*, 1051; *A.*, 1916, ii, 598.
[49] *Ibid.*, 1107; *A.*, ii, 12.
[50] *Ibid.*, 1359; *A.*, ii, 64; compare also *Mem. Manchester Phil. Soc.*, 1916, **60**, No. 11; *A.*, ii, 290.

the formation of definite compounds by combination of the discharged hydrogen with the metal of the cathode. These hydrides are unstable, endothermic compounds with a high solution pressure which is supposed to be the immediate cause of the overvoltage effect.

It is suggested that the hydrides which show the group overvoltage are the lowest formed by the metals in each group, and that the addition of an atom of hydrogen to any hydride changes the overvoltage to the value which is characteristic of the preceding group. In other words, the solution pressures of the hydrides are determined by the number of unsaturated valency bonds. When no hydride is formed, the metal behaves as a hydrogen electrode, this behaviour being exhibited most clearly by the platinum metals.

Although the anodic overvoltages do not show quite the same degree of regularity, the theory would, in the same way, attribute anodic overvoltage to the formation of unstable oxides. As is well known, the formation of oxide films forms the basis of Faraday's theory of the passive state, and according to the theory under discussion, passivity may be expected when the oxides formed are good conductors of electricity and at the same time are relatively insoluble in the electrolyte solution. If, on the other hand, the oxides are poor conductors and insoluble, the conditions are favourable to the manifestation of valve action. The theory thus correlates a number of otherwise disconnected facts, overvoltage effects being connected up with passivation, valve action, and also with the periodicity which is exhibited in electrolytic passivation in certain circumstances.

Chemical Dynamics.

The theory that neutral molecules are much less reactive than electrically charged ions was at one time in considerable favour, but this view is not warranted by the results of a large amount of recent work on the mechanism of reactions. The kinetic investigation of reactions of various types has, in fact, shown that the reactivity of molecules is very frequently of the same order as that of the corresponding ions, and in some cases the molecule appears to be the more reactive form. When electrolytes react in both these forms, the actual progress of the reaction represents the additive effect of molecular and ionic activity, but the relative activities can readily be deduced from the results of experiments in which the concentration of the electrolyte is varied.

Recent work of Acree and his collaborators, who have furnished

a large body of evidence in support of the dual activity of electrolytes, indicates that the ratio of the activities of the molecular and ionic forms of a substance is not independent of the reaction in which the substance takes part. A comparison of the results obtained for the alkali metal ethoxides in the inversion of *l*-menthone[51] and in the action on methyl iodide[52] reveals a considerable difference in the ratio of the activity of the non-ionised ethoxide to that of the ethoxide ion. A similar variation has been previously noted in the action of acids as catalysts. On the other hand, recent measurements[53] of the rate of transformation of γ-hydroxyvaleric acid into valerolactone with hydrochloric acid as catalyst have given a value for the activity ratio which is the same as that found for the acid when used as catalyst in the hydrolysis of ethyl acetate.[54]

Experiments on the catalysing power of a series of strong acids[55] show that the activity of the non-ionised acid is in all cases greater than that of the hydrogen ion. The catalysing power of the non-ionised acid decreases in the order hydrochloric, hydrobromic, trichloroacetic, *p*-toluenesulponic, trichlorobutyric acid. In the case of the last-mentioned acid, the ratio of molecular to ionic activity is nearly equal to unity, and the catalysing power is consequently determined solely by the concentration of the acid and is independent of its degree of ionisation. The results obtained for the inversion of *l*-menthone by lithium ethoxide show also that this electrolyte is equally active in the ionised and non-ionised forms.[56]

The facts established by G. Senter in his investigations of the mechanism of the reactions between halogen-substituted acids or their salts and water or alkali hydroxides[57] not only afford evidence of the composite nature of these reactions and of the identity of the reacting molecular species, but have an additional interest in that they have been applied[58] in the further examination of the phenomenon usually referred to as the Walden inversion. It seems quite plausible to assume that the optical character of the product, which is obtained by replacement of the halogen in an optically

[51] W. A. Gruse and S. F. Acree, *J. Amer. Chem. Soc.*, 1917, **39**, 376; *A.*, ii, 251.

[52] B. M. Brown and S. F. Acree, *ibid.*, 1916, **38**, 2145; *A.*, ii, 24.

[53] H. S. Taylor and H. W. Close, *ibid.*, 1917, **39**, 422; *A.*, ii, 253.

[54] H. S. Taylor, *ibid.*, 1915, **37**, 551; *A.*, 1915, ii, 248.

[55] H. M. Dawson and T. W. Crann, *T.*, 1916, **109**, 1262; *A.*, ii, 26.

[56] W. A. Gruse and S. F. Acree, *loc. cit.*

[57] Compare G. Senter and H. Wood, *T.*, 1916, **109**, 681; *A.*, 1916, ii, 523, and previous papers.

[58] Compare G. Senter and G. H. Martin, *ibid.*, 1917, **111**, 447; *A.*, ii, 447, and previous papers.

active organic acid by the hydroxyl or amino-group, may vary according to whether the substitution has been effected in the non-ionised molecule or in the corresponding anion. The fact that the sign of the product is influenced by the nature of the medium in which the reaction takes place[59] is doubtless capable of explanation on similar lines, and sufficient evidence has already been obtained to warrant the conclusion that the problem of the Walden inversion will probably find a solution on the lines of Senter's kinetic investigations.

The experimental study of certain reactions has been much facilitated[60] by the use of regulator mixtures. These mixtures are frequently employed for the production of aqueous solutions which have a well-defined hydrogen ion concentration, and by making use of them in kinetic experiments it is possible to maintain the active mass of one or other of the reacting substances constant, and thereby to prevent disturbances such as would arise from a tendency to reversal or from the auto-catalytic influence of the products of reaction.

According to Skrabal,[61] such regulator mixtures are to be distinguished according to whether they act as static or as dynamic regulators. This distinction is based on the difference in the rapidity with which any disturbance of the equilibrium between the components of the regulator mixture is nullified. In its control of the hydrogen ion concentration, a mixture of sodium dihydrogen phosphate and disodium hydrogen phosphate behaves as a static regulator, whilst a mixture of potassium iodide and iodate behaves as a dynamic regulator. The dynamic course of a particular reaction varies according to whether the reaction is controlled by a static or by a dynamic regulator, but the results obtained in the investigation of the rate of hydrolysis of certain esters[62] show that both lead to the same value for the velocity-coefficient of the controlled reaction.

According to observations[63] on the rate of hydrolysis of dialkyl carbonates, this reaction proceeds at a conveniently measurable rate in a solution of sodium carbonate, whereas the corresponding sodium alkyl carbonates are hydrolysed with immeasurable rapidity whether the solution is alkaline or acid. The anomalies afforded by these kinetic observations have led to the suggestion

[59] G. Senter and H. D. K. Drew, *T.*, 1915, **107**, 638; *A.*, 1915, i, 535; *T.*, 1916, **109**, 1091; *A.*, 1916, i, 815.

[60] Compare A. Skrabal, *Monatsh.*, 1917, **38**, 29; *A.*, ii, 250; A. Skrabal and A. Sperk, *ibid.*, 1917, **38**, 191.

[61] *Monatsh.*, 1917, **38**, 159.

[62] A. Skrabal, *ibid.*, 180.

[63] *Ibid.*, 305.

that the second stage in the hydrolysis of the carbonic esters is not really a hydrolytic process, but an intramolecular change represented by the formula $CO<^{OH}_{OR} \longrightarrow CO_2 + ROH$.

The dehydration of certain crystalline hydrates has been found to show irregularities in the initial stages, the effect being equivalent to a period of induction. Experiments made with copper sulphate pentahydrate[64] show that the crystals have at first a much smaller tendency to give up water than in the later stages, in which the progress is in accordance with the requirements of the law of probability. Mechanical stirring of the finely powdered crystals, and the presence of crystals of the trihydrate, tend to obliterate the induction period, and in general the facts suggest a close analogy with the behaviour of supersaturated solutions. If this view is correct, it may be that the induction period is to be explained in terms of the relatively high vapour pressure of very small particles of the trihydrate, and in that case it is unnecessary to assume the intermediate formation of an unstable amorphous form[65] in order to account for the changes in the vapour pressures of crystalline hydrates.

It has been proposed[66] that the usual method of recording the velocity of reactions should be modified by substituting for the velocity-coefficient (k) a number the significance of which can be more readily visualised. If the unit of time is so chosen that $k=1$, then this unit of time (t) affords a direct indication of the speed of the reaction for unit concentration of the reacting substances. If, for instance, $k=0{\cdot}02$ (time in minutes), then $t=50$ minutes, which signifies that one gram-molecule of the substances will react in 50 minutes when the concentration is equal to unity.

The radiation hypothesis of chemical reactivity has been further developed, and it is shown[67] that the idea that molecules become reactive when the energy content reaches a certain critical value is quite compatible with the fact that the reaction may be accompanied by the absorption or liberation of heat. In the simplest case of a unimolecular reversible change, the connexion between the heat of reaction, Q_v, and the critical increments of the two kinds of molecules, E_1 and E_2, is given by the equation $Q_v=E_2-E_1$, which by introduction of the quantum hypothesis assumes the form $Q_v=Nh(\nu_2-\nu_1)$, in which ν_1 and ν_2 are the

[64] W. N. Rae, *T.*, 1916, **109**, 1229; *A.*, ii, 24.
[65] J. R. Partington, *ibid.*, 1911, **99**, 466.
[66] J. W. McBain, *Trans. Faraday Soc.*, 1917, **13**.
[67] W. C. M. Lewis, *T.*, 1917, **111**, 457; *A.*, ii, 302.

critical frequencies of the reacting substances. The latter equation is found to hold for a number of high-temperature reactions.[68]

Chemical Equilibrium.

There is a good deal of evidence to show that the equilibrium in a reversible system varies with the nature of the solvent. The displacement of the equilibrium in passing from one solvent to another must be ascribed to a difference in the heat of reaction in the two solvents, and this, in its turn, may be referred to differences in the heats of dissolution of the reacting substances in the solvents in question.[69] If the reversible reaction is represented by $A \rightleftharpoons B$, and Q_A and Q'_A are the heats of dissolution of A in two different solvents, the corresponding values for B being Q_B and Q'_B then the relation between the equilibrium constants K and K' is given by $\log K/K' = (Q_A - Q'_A) - (Q_B - Q'_B)/RT$. In such systems, the solvent cannot be supposed to play the part of a catalyst when this is defined in the usual way.

In an interesting contribution to the question of the influence of temperature on chemical equilibrium, F. E. C. Scheffer[70] has arrived at the conclusion that the accuracy attained in the investigation of gaseous equilibria, and more particularly equilibria at higher temperatures, does not warrant the use of the relatively complicated formulæ which are frequently employed to represent the dependence of the equilibrium on the temperature.

The fundamental thermodynamic equation is

$$d \log K/dT = -Q/RT^2,$$

and by making different assumptions in regard to the influence of the temperature on the heat of reaction, this differential equation leads to various integrated forms, which may be directly employed in testing the experimental observations.

If the heat of reaction is independent of the temperature, which is equivalent to the assumption that the algebraic sum of the heat capacities of the reacting substances is zero, then $Q = a$ and $\log K = a/T + b$ (1). If the algebraic sum of the heat capacities is not zero, but has a constant value independent of the temperature, then $Q = a + bT$ and $\log K = a/T - b \log T + c$ (2). If, again, the sum of the heat capacities is a linear function of the temperature, then $Q = a + bT + cT^2$ and $\log K = a/T - b \log T - cT + d$ (3).

Scheffer's investigation of the available data relative to gaseous

[68] W. C. M. Lewis, *T.*, 1917, **111**, 1086.

[69] A. Smits, *Proc. K. Akad. Wetensch. Amsterdam*, 1917, **19**, 708; *A.*, ii, 171.

[70] *Ibid.*, 636; *A.*, ii, 170.

equilibria at high temperatures has shown that, in almost every case, the influence of temperature can be adequately represented by the simplest equation. The dissociation of hydrogen iodide may be quoted as an example. According to Bodenstein, his observations between 550° and 800° are satisfactorily represented by equation (3), but, as Scheffer points out, this formula fails to reproduce Steigmüller's observations for the temperature interval 300—350°, whereas the simple equation (1) represents the experimental data for both intervals of temperature quite satisfactorily.

Theoretical considerations relative to the influence of temperature on chemical equilibrium also lead to the conclusion that the data for systems, in which solids react with gases, are not nearly as accurate as a cursory examination would suggest. The data obtained in the investigation of certain systems of this type point to the existence of a maximum or minimum value of K at a particular temperature. On the assumption that this is a real effect, it is obvious that equation (1) cannot represent the influence of temperature on the equilibrium, for this equation does not admit of a maximum or a minimum in the value of the constant K.

According to the recorded data[71] for the equilibrium in the system $Fe + CO_2 \rightleftarrows FeO + CO$, the equilibrium constant has a minimum value at 680°. At this temperature $Q = 0$, whilst at 585° $Q = -3110$ cals. and at 835° $Q = +8720$ cals. This difference of 11,830 cals. in the heat of reaction for a change of temperature of 250° corresponds with a difference of 47·3 in the algebraic sum of the molecular heats of the substances taking part in the reaction. Since the difference between the heat capacities of the substances on opposite sides of the equation is solely due to differences in the mode of combination of the elements and the effect of this rearrangement is known to be small, it appears legitimate to conclude that the experimental data are untrustworthy.

This example may suffice to indicate that the analysis of equilibrium data, according to Scheffer's method, affords a valuable criterion in arriving at an estimate of the degree of trustworthiness of data which purport to show the influence of temperature on the equilibrium.

Electrical Ignition of Gaseous Mixtures.

An extensive series of observations[72] on the ignition of inflammable mixtures of gases under the influence of condenser

[71] E. Baur and A. Glaessner, *Zeitsch. physikal. Chem.*, 1903, **43**, 354; *A.*, 1903, ii, 423.

[72] W. M. Thornton, *Proc. Roy. Soc.*, 1914, [A], **90**, 272; *A.*, 1914, ii, 524; *ibid.*, 1914, [A], **91**, 17; *A.*, 1914, ii, 834; compare also *ibid.*, 1916, [A], **92**, 381; *A.*, 1916, ii, 306.

spark or impulsive electric discharge has led W. M. Thornton to the conclusion that the minimum energy required for ignition, changes in a discontinuous manner with the composition of the gas mixture. For mixtures of air with methane, ethane, propane, carbon monoxide, hydrogen sulphide, and hydrogen, the curves which are obtained by plotting the energy of the least igniting current against the composition are characterised by one or more breaks or steps, which correspond with sudden changes in the ease of ignition as the composition of the gas mixture passes through certain critical stages. These critical mixtures are said to be distinguished by the fact that the ratio of the number of the oxygen atoms to the number of the molecules of inflammable gas is represented by a whole number. In a further paper,[73] it is claimed that simple molecular relations of the same kind obtain for those mixtures which correspond with the upper and lower limits of inflammability.

If it were definitely established that stepped ignition phenomena are really characteristic of the electrical ignition of inflammable gaseous mixtures, the observation would obviously be of considerable theoretical significance. More recent experiments by R. V. Wheeler and his collaborators have, however, failed to confirm the existence of such effects as have been described by Thornton.

In the course of attempts[74] to repeat the observations on the effect of the impulsive discharge from the secondary circuit of an inductive coil, it was found that comparative results could only be obtained when the rate of break of the primary circuit and the condition of the secondary spark-gap were rigidly controlled. Under these conditions, experiments with mixtures of methane and air and of hydrogen and air gave perfectly smooth curves showing no sign of discontinuity with change in composition.

According to Thornton, discontinuities are also met with in the ignition of a given mixture under different pressures,[75] but Wheeler's observations on a mixture of methane and air, in which the electrical conditions were adequately controlled, gave a perfectly continuous curve for a change in pressure from 100 to 800 mm.[76] Experiments at higher pressures[77] (500 to 5000 mm.) gave the same result. In the course of these experiments it was noted that the least discharge which could pass across a 1 mm. gap was sufficient to cause ignition, and it was found necessary to diminish the width of the gap in order to obtain comparative

[73] *Phil. Mag.*, 1917, [vi], **33**, 190; *A.*, ii, 172.
[74] S. G. Sastry, *T.*, 1916, **109**, 523; *A.*, 1916, ii, 381.
[75] *Colliery Guardian*, 1916, **112**, 503.
[76] *T.*, 1917, **111**, 130; *A.*, ii, 171.
[77] *Ibid.*, 411; *A.*, ii, 300

measures of the least igniting current. This fact, according to Wheeler, offers a possible explanation of the discrepancy between the two series of experiments, in that Thornton's experimental arrangement merely affords a measure of the influence of the composition or of the pressure of the gas on the readiness with which the discharge takes place across the spark-gap. This seems to be quite a reaonable interpretation of the divergence, and although it is just possible that some unknown factor is responsible for the difference, the evidence is in favour of the view that ignition curves are continuous in type, and that there is no satisfactory experimental basis for the theory of stepped ignition.

A novel method for the determination of ignition-temperatures has been described,[78] in which the gaseous mixture, contained in a small soap bubble, is ignited by contact with an electrically heated wire or other red hot body, the temperature being noted at which ignition just takes place. The ignition-temperatures, which have been obtained for various mixtures of inflammable gases with air by the use of this method, are for the most part appreciably higher than those given by the methods which have been employed in previous experiments. The discrepancy is said to be due to the circumstance that, in the older methods, slow combustion precedes the actual ignition and generates sufficient heat to raise the residual mixture to its ignition point. In other words, the older methods involve a time factor which must be eliminated if correct values are to be obtained for the ignition-temperatures. It is claimed that this is accomplished by the soap-bubble method, which is said to be eminently suitable for comparative observations and to permit of fixing the ignition-point with a considerable degree of accuracy.

It is a well-known fact that, under certain conditions, mixtures of inflammable gases and air show an effect which has been described as the "uniform movement," in which the flame produced by ignition of the mixture travels with uniform speed for a considerable distance from the point of ignition. The conditions most favourable for this effect are that the inflammable mixture should be contained in a long horizontal tube, open at one end and closed at the other, and that ignition should be effected near the open end of the tube by a source of heat not much higher in temperature than the ignition-point, and not productive of mechanical disturbance in the mixture. According to Mallard and Le Chatelier, the speed of the uniform movement for a given gaseous mixture is not appreciably affected by the cooling of the hot gases by the walls of the tube when the diameter of the tube is sufficiently great, and it has been supposed that the speed of the uniform movement in

[78] J. W. McDavid, *T.*, 1917, **111**, 1003.

moderately wide tubes (5—10 cm. diameter) at the ordinary pressure is determined solely by the nature of the gaseous mixture.

According to recent measurements [79] in tubes varying from 2·5 to 100 cm. in diameter, this is not the case, but the velocity increases continuously with increase in the width of the tube. In very wide tubes, the effect is accompanied by a turbulence of the flame front, which is due to the upward movement of the hot gases by convection. It is evident from these observations that the speed of the uniform movement does not possess the attributes which would entitle it to be regarded as a characteristic property of a combustible mixture, and further that the uniform movement is a strictly limited phenomenon which can only be observed in tubes which are wide enough to prevent appreciable cooling and yet narrow enough to suppress the influence of convection currents.

The theoretical considerations advanced by Mallard and Le Chatelier,[80] lead to the conclusion that for mixtures which have approximately the same thermal conductivity, the speed of the uniform movement should be proportional to $(T-t)/(t-\theta)$, where T is the combustion temperature, t the ignition-temperature, and θ the initial temperature of the combustible mixture. By experiments on mixtures of methane, oxygen, and nitrogen, Mason and Wheeler have shown that this relation is satisfied, provided that the amount of oxygen in the mixture is in excess of that required for complete combustion. For mixtures which contain less oxygen, the observed speed has a lower value, and this is probably due to the relatively slow rate of the combustion, resulting in a greater loss of heat through the walls of the tube.

Colloids.

The ageing of colloidal solutions is attended by changes in various properties, such as the viscosity, the readiness with which the sols gelatinise, and their sensitiveness towards electrolytes which have a coagulating action. It has been generally supposed that these irreversible ageing effects are due to the gradual formation of larger particles by a process of aggregation.

In some interesting observations [81] on colloidal solutions of ceric hydroxide it has been found that the ageing process is very largely modified when the sols are subjected to the action of β- or γ-rays. The first effect produced by the rays consists in an increase in the normal rate of diminution in the viscosity, but this effect is rapidly superseded by a second, in which the viscosity increases continu-

[79] W. Mason and R. V. Wheeler, *T.*, 1917, **111**, 1044.
[80] *Ann. des Mines*, 1883, [viii], **4**, 274.
[81] A. Fernau and W. Pauli, *Kolloid Zeitsch.*, 1917, **20**, 20; *A.*, ii, 189.

ously to a value which is very large in comparison with that of the freshly dialysed sol, the final result of this process being the formation of a stable jelly. If the exposure to the active rays is made intermittent, the course of the viscosity–time curve is of the same type. Furthermore, it has been found that if the active rays are cut off before the viscosity has reached a minimum, the ageing is still characterised by the second stage, in which the viscosity increases, but in these circumstances the viscosity reaches a maximum, and subsequently decreases almost as rapidly as it increased in the second stage.

The effects described are supposed to be connected with changes in the degree of hydration of the colloidal hydroxide. Under the influence of β- or γ-rays the charge carried by the colloidal particles is neutralised, and this process is accompanied by a diminution in the degree of hydration and in the viscosity. The subsequent increase in the viscosity in the second stage of the ageing process is attributed to the aggregation of the neutral particles, a process which takes place with a velocity comparable with that of crystallisation and similar processes. To account for the maximum viscosity and the subsequent decrease which are observed when the time of exposure to the active rays is comparatively short, it is suggested that this may be due to the peptonising action of the charged particles which are enclosed in the jelly resulting from the aggregation of the neutral particles. Evidence of the plausibility of this explanation is afforded by the fact that ceric hydroxide jellies are readily peptonised when the corresponding sol form is added to the jelly.

The above observations are of particular interest in that they appear to throw new light on the mechanism of the coagulation process. It has, in fact, been found that similar changes in the viscosity of ceric hydroxide sols occur when very small quantities of electrolytes are added to the colloidal solutions. The parallelism is not quite complete, for the time factor is different in the two cases, and the jellies produced by the action of electrolytes are unstable, but the similarity is sufficiently pronounced to justify the conclusion that the successive changes which occur in the colloidal particles are probably the same.

In connexion with the ageing of colloids, a short reference may be made to certain observations,[82] which have been made on the metal and salt films which condense on the wall of a metallic filament lamp when the metal or salt in question is vaporised from the surface of the filament by the passage of a current. The film of

[82] W. Reinders and L. Hamburger, *Proc. K. Akad. Wetensch. Amsterdam*, 1917, **19**, 958; *A.*, ii, 405.

sodium chloride, which is obtained under these conditions, appears to be quite devoid of structure when examined by the ultra-microscope. On exposure to moist air the film quickly becomes opalescent, and at this stage the ultra-microscope shows the presence of a network of ultra-microns. With time, the network becomes coarser, and ultimately it is possible to recognise the presence of cubic microcrystals. If the sodium chloride film is covered by Canada balsam, the vitreous condition may be preserved indefinitely. Metallic films of similar character have been prepared, but these are much less stable than vitreous sodium chloride.

Structure of Jellies.

The various theories advanced in explanation of the characteristic properties of jellies have not led to any generally accepted view of jelly structure. As the result of ultra-microscopic observations, the theory has been recently advanced [83] that gelatin contains two substances, α- and β-gelatin. The α-gelatin forms the structural units, and consists of an irregular network of fibrils, whilst β-gelatin is structureless and fills the spaces in the network. The fibrillar network is not visible in an ordinary gelatin jelly, but the structure becomes evident when the gelatin is subjected to the action of agents which remove the β-gelatin to a greater or less extent. In these circumstances, the elementary fibrils undergo orientation, forming groups which are visible in the ultra-microscope.

This theory of jelly structure is made the basis of an attempt [84] to explain the laminated structures, familiar under the name of Liesegang's rings, which make their appearance when an aqueous solution of an electrolyte is brought into contact with a jelly impregnated with a second electrolyte, which reacts with the first to form an insoluble compound. It is now shown that rhythmic structures are developed in the jelly when the diffusing substances do not react chemically, and, in fact, the evidence brought forward seems to indicate that the diffusion of any electrolyte from an aqueous solution into a jelly gives rise to laminated structures. It is said that these facts cannot be accounted for by the various theories which have been advanced in explanation of the formation of Liesegang's rings, and that the laminated appearances are primarily due to the jelly structure. The rate of diffusion of an electrolyte into a jelly will depend on the orientation of the structural fibrillar elements, and forces are thus called into play which give to the system a more or less well-defined laminated appearance.

[83] W. Moeller, *Kolloid Zeitsch.*, 1916, **19**, 205, 213; *A.*, ii, 132.
[84] *Ibid.*, 1917, **20**, 242; *A.*, ii, 410; *ibid.*, 1917, **20**, 257; *A.*, ii, 454.

Swelling of Colloids.

Although sporadic attempts have been made to correlate and explain various phenomena which are associated with the swelling of colloids, and to ascertain the factors on which the swelling depends and the laws which govern the process, it cannot be said that our present knowledge of the subject is in any way commensurate with the importance of the phenomenon in its bearing on biochemical problems and on processes connected with the textile and other industries. The elimination of secondary disturbances constitutes one of the chief difficulties of the experimental investigation of the question, and the fact that this point has received adequate consideration imparts a special value to the results obtained in recent experiments.[85] The substances chosen for investigation were pure chemical compounds, the swelling of which is not complicated by capillary absorption effects, by the formation of compounds with the swelling liquid, or by the irreversibility of the process.

For various substances of this character it has been found that the relation between the degree of swelling, measured by the ratio of the weight of the absorbed water to the weight of the dry substance, and other properties, is independent of the chemical nature of the swelling substance. The curves which show the relation between the vapour pressure, the heat of swelling, the volume change, and the heat capacity on the one hand, and the degree of swelling on the other, are, moreover, quite similar to the corresponding curves for mixtures of water with non-volatile liquids, such as sulphuric acid, phosphoric acid, and glycerol. This similarity suggests that the swelling process, when free from secondary disturbances, is to be regarded as the formation of a solid solution of water in the swelling substance. This idea is incompatible with the micellary hypothesis put forward by Nägeli to explain the behaviour of swelling substances; it disposes of the necessity for the assumption of complex structural units and replaces these by molecules.

H. M. Dawson.

[85] J. R. Katz, *Koll. Chem. Beihefte*, 1917, **9**, 1; *A.*, ii, 245.

INORGANIC CHEMISTRY.

The past year has been marked by a very considerable reduction in the number of papers that have come under review. This decrease is more pronounced in those papers which deal with the determination of atomic weights and with the more theoretical side of inorganic chemistry.

Among the latter, however, is one which perhaps merits more than a passing notice, namely, Professor Harkins's paper on the genetic relationship between the atoms. There is no doubt that radioactivity, together with the discovery of the existence of isotopes, has reawakened an interest in the question of the genesis of the elements. The conception of the hydrogen–helium structure of all atoms with an atomic weight greater than 4 was first enunciated two years ago, and the evidence in its favour is so remarkably convincing that it surely must receive earnest consideration by all chemists.

The papers which deal with the preparative side of inorganic chemistry show but little decrease in number, and, in general, it may be said that the work carried out during the past twelve months exhibits more than the usual interest.

Atomic Weights.

The past year has been remarkable in the fact that much less work has been published on the determination of atomic weights than during the preceding year. The International Committee direct particular attention to this, and point out that it is due in the main to the entry of America into the war, for it is in this country that so many important atomic weight determinations have been carried out in recent years. No change in the values as adopted for 1917 has been recommended by the Committee, and, indeed, the Committee has decided to intermit its annual reports.

Attention may be directed to a suggestive paper dealing with the genetic relationship between the atoms of the elements.[1] In

[1] W. D. Harkins, *J. Amer. Chem. Soc.*, 1917, **39**, 856; *A.*, ii, 303.

previous papers on this subject, it has been suggested that the elements are intra-atomic compounds of hydrogen.[2,3] The hydrogen first becomes helium, and this becomes a secondary unit of fundamental importance in the formation of all the elements with atomic weights greater than its own. The ninety-one known elements, other than hydrogen, fall into two series. At any rate, among the elements of low atomic weight, the atoms having even atomic numbers are in general built up of helium atoms, and therefore may be said to have the general formula nHe', whilst those having odd atomic numbers seem to have the general formula $nHe' + H'_3$, these formulæ representing intra-atomic, and not chemical compounds. If the elements actually belong in two series, as the hypothesis indicates, then the distinction between the two should be apparent in at least one fact concerning the respective elements. It was shown in the previous papers that the atomic weights of the elements, interpreted in the light of the method by which radioactive elements disintegrate, give almost conclusive evidence in favour of the theory. Extremely striking additional evidence is now adduced in support of this hypothesis. The ordinary periodic system appears to be a relationship which expresses graphically the variation in the arrangement and the number of external electrons, especially the valency electrons, in the atom, which finds its expression in the chemical and physical properties of the element. The hydrogen–helium system is most fundamentally related to the structure of the nuclei of the atoms, and this structure should not affect the arrangement of the external electrons if the nucleus is extremely minute, since this arrangement would depend on the number of electrons, which in turn depend on the nuclear charge, but not on the internal structure of the nucleus except in so far as this structure affects the total charge. The structure of the nucleus should, however, affect its stability, which would have an expression in the abundance of the respective elements. There is another factor, too, which would have an effect on the abundance, and that is the relative abundance of the special materials used in the formation of the element in question. The abundance of the elements in the earth's crust might seem to give the best information in this respect if it were not known that the surface of the earth has been subjected to very long-continued differentiative processes, and so has a very local character. The meteorites, on the other hand, come from much more varied positions in space, and at the same time show

[2] W. D. Harkins and E. D. Wilson, *J. Amer. Chem. Soc.*, 1915, **37**, 1367, 1383, 1396; *A.*, 1915, ii, 543, 544.

[3] W. D. Harkins and R. E. Hall, *ibid.*, 1916, **38**, 169; *A.*, 1916, ii, 241,

much less indication of differentiation. In the meteorites, the elements of even atomic numbers on the average are about seventy times more abundant than the odd-numbered elements, and, moreover, if the elements are plotted in the order of their atomic numbers, it is found that the even-numbered elements are in every case very much more abundant than the adjacent odd-numbered elements. Almost more striking than this is the fact that the first seven elements, in the order of their abundance, are all even-numbered, and, furthermore, make up 98·78 per cent. of the material. Both the iron and the stone meteorites separately show the same relations. Thus the stone meteorites contain 97·6 per cent. and the iron meteorites 99·2 per cent. of even-numbered elements. It is remarkable that the highest percentage found for any odd-numbered element in any class of meteorites is 1·53, whilst among the even-numbered elements larger percentages are common and range even as high as 90·6 per cent. In the lithosphere, whilst the relationship is not so striking, the even-numbered elements are still seven to ten times as abundant as those which are odd, depending on whether the calculations are made by weight or by atomic percentage. Among the rare earths, the even-numbered elements are the more abundant. Among the radioactive elements, the odd-numbered element is in each case either of a shorter period than the even-numbered or else as yet undiscovered. All the five unknown elements are of odd numbers. The elements of low atomic numbers are found to be much more abundant than those of higher atomic number, both in meteorites and on the earth. Thus the first twenty-nine elements make up about 99·9 per cent. of the material, while the remaining sixty-three are either extremely rare or comparatively rare.

The above results seem to show that the elements fall into two series, as predicted from the hydrogen–helium structure hypothesis. The variation in the abundance of elements would seem to be the result of an atomic evolution, which is entirely independent of the Mendeléev periodic system. The formation of the elements seems to be, however, related to the atomic number. The hydrogen–helium structure of the atoms is seen to be on as firm a basis as a large number of the ideas of physics or chemistry which are accepted without question, since the predictions originally made have been verified in so striking a way. The first prediction was that the elements of low atomic number would be found to show evidences in their atomic weights that their atoms are built up according to the general plan, in relation to which the radioactive elements (of high atomic weight) disintegrate. The second prediction was that the elements of even atomic number would show

a marked difference in abundance from those of odd atomic number. The agreement with both these predictions is very much more striking than was at first expected, and this agreement involves such a large number of data that it is on this account even the more remarkable.

In general reference to the stability of the elements, it is to be expected that the composition of the nucleus should affect its own stability, which from radioactive evidence means the stability of the atom. From this point of view, it is reasonable to suppose that the atoms of one of the series, the even or the odd, should be more stable than those of the other. There is at least one other factor than stability which must be considered in this connexion. Since the formula for the odd-numbered elements is $nHe' + H'_3$, it is evident that, if the supply of H_3 was relatively small at the time of formation, not so much material would go into this system. This would be true whether the H_3 represents three atoms of hydrogen or one atom of some other element. With regard to the latter alternative, it is at least remarkable that the H_3 occurs eleven times in the system for the first twenty-seven elements, whilst H_2 and H each only occurs once, and it may also be mentioned that the atomic weight of nebulium has been determined by interference methods to be 2·7, and this is believed to indicate a real atomic weight of 3.[4]

It has been shown in support of the above theory that in the case of the elements with atomic numbers 81 to 92, the number of known isotopes in a pleiad and the character of the predominant radiation show a periodic variation of the type to be expected from the theory.[5] It appears that the isotopes of even-numbered elements are more numerous than those of odd-numbered elements. The former show a well-marked tendency to undergo disintegration with the emission of α-rays rather than of β-rays. These facts accord with the hydrogen–helium hypothesis.

Phosphorescence.

An important paper has been published dealing with the phosphorescence of zinc sulphide, which especially treats of the effect of various impurities on the brilliancy and also on the nature of the illumination.[6] One statement in this paper is so categorically opposed to the now generally accepted theories of this phenomenon

[4] C. Fabry and H. Buisson, *Astrophys. J.*, 1914, **40**, 256.

[5] N. F. Hall, *J. Amer. Chem. Soc.*, 1917, **39**, 1616; *A.*, ii, 438.

[6] Miss E. MacDougall, A. W. Stewart, and R. Wright, *T.*, 1917, **111**, 663; *A.*, ii, 471.

that it is worthy of careful consideration. In general, it might be considered that phosphorescence is a physical phenomenon, and hence can scarcely find a place in a discussion of recent advances in inorganic chemistry, but the principle involved is one of great importance to inorganic chemists, and more particularly to those engaged in work on the rare earths. The statement in question is that pure zinc sulphide, when suitably treated, exhibits phosphorescence. Now it would seem to be established beyond any question of doubt by the work of Lenard and Klatt,[7] and by Urbain and Brüninghaus,[8] that it is a cardinal principle of this phenomenon that no pure substance phosphoresces, and that phosphorescence is essentially a property of diluted matter. The phenomenon of phosphorescence is one of the most valuable adjuncts to work on the rare earths, for it is one of the most stringent tests known as to the individuality of a rare earth. The method of work employed by the French school is the fractionation of a mixture of rare earths by some suitable method. The equivalents of the successive fractions are determined, and these are plotted on a graph against the numbers of the fractions. As the work proceeds, the curve shows flat portions, due to the separation of definite individuals or of mixtures which cannot be separated by the method adopted. In order to determine whether the fractions with constant equivalents contain one individual or a mixture, their power of phosphorescing is tested. If any phosphorescence is exhibited, then it is known that the substance is a mixture and not one single individual. It follows, therefore, that, if it be established that a pure substance can phosphoresce, then grave doubt is at once thrown on the whole of the work of the German and the French schools. Very great care should be taken to test in the most rigid way possible the absence of any impurity before such a statement is made that pure zinc sulphide phosphoresces. As an example of the phosphorescence of a so-called pure material may be quoted the case of lime prepared from calcite. It certainly might be thought that in this case the phosphorescence is that of a pure substance. It was proved, however, that the luminescence is in reality due to the presence of traces of manganese. A second instance, now almost classic, is Crookes's work on samarium and the citron band of phosphorescence. By the adoption of a suitable method of fractionation, it was found possible to obtain fractions which at first showed this band with increased intensity. A continuation of this separation produced a material which suddenly lost its power of phosphorescing, a

[7] P. Lenard and V. Klatt, *Ann. Physik.*, 1904, [iv], **15**, 225, 425, 633.
[8] G. Urbain, *Ann. Chim. Phys.*, 1909, [viii], **18**, 222, 289.

startling enough result until the explanation was forthcoming in that pure samaria does not phosphoresce.

It would seem that in the case of the zinc sulphide the authors did not take any absolutely rigid precautions against the presence of any impurity in the samples examined. Possibly they were not aware of the fundamental importance of their statement that the pure zinc sulphide does show luminescence. It is to be hoped that this statement will not be accepted as proven until the most rigid precautions have been taken, and that the authors themselves will be able further to investigate the phenomenon from the particular point of view of the total absence of all impurity. It would indeed seem that the variation observed by them in the phosphorescence caused by added impurity is in itself evidence that the luminescence is due to the presence of impurities hitherto unrecognised.

This must not in any way be considered as an adverse criticism of the work under discussion, which in general forms a distinct contribution to the literature on the phosphorescence of inorganic salts. At the same time, the section of the paper dealing with the phosphorescence of pure zinc sulphide is so brief that one cannot believe that the authors were aware that their statement, if true, would controvert the results of very many years' work carried out with the most extraordinary care by the German physicists and the French chemists.

Exactly the same criticism must be made of a similar statement regarding magnesium sulphide, and in this case the author claims specifically to have prepared pure magnesium sulphide and to have observed the phosphorescence.[9] The compound was made by passing a stream of hydrogen and sulphur vapour over red-hot granular magnesium. In this way, a crude product was obtained containing 30 to 50 per cent. of sulphur. The free metal in the crude sulphide was removed by distillation at 600—700° in the vacuum of a mercury pump, or by adding bromobenzene to an ethereal suspension, the sulphide being quite unaffected. Pure magnesium sulphide is stated to have been prepared in this way, but it is very questionable whether any trust can be placed in the statement that pure magnesium sulphide shows phosphorescence when such a statement is based on the phenomena exhibited by a compound prepared in the above way. In the first place, it is legitimate to ask whether the magnesium used was absolutely pure and whether the hydrogen and sulphur were free from all suspicion of impurity. What evidence is there that no impurity was derived from the bromobenzene or the ether in the one case or from the mercury

[9] E. Tiede, *Ber.*, 1916, **49**, 1745; *A.*, 1916, ii, 619.

vapour in the other? This evidence can carry no conviction that such an important discovery has been made as that an absolutely pure chemical individual shows phosphorescence.

Valency.

In this section, few papers have been published. Ephraim has extended his observations on the formation of addition complexes and their dissociation pressures, but consideration of these may be postponed until the theoretical developments are more complete.

Mention may, however, be made of a paper on the structure of inorganic compounds which presents points of some interest.[10] The view had already been put forward that every element possesses positive and negative affinity, and that atoms may be united to each other by one of these or by both at the same time. In the former case, ionisable atoms are formed, due to one affinity being free and therefore able to combine with the solvent. In the latter case, non-polar compounds are produced, such as methane and carbon tetrachloride. Since the elements, for example, copper and cobalt, do not combine with ammonia, they do not possess negative affinity. On the other hand, in their salts, having lost electrons, they develop negative affinity, and hence they can combine with ammonia. The more electrons lost, the greater the negative affinity, this being shown by the fact that the cobaltic hexammines are more stable than the cobaltous hexammines, and that cuprous chloride only combines with three molecules of ammonia, whilst cupric chloride combines with six molecules of ammonia. In general, three types of chemical combination are recognised.

(1) Combination due to the saturation of primary affinity only, which gives strong electrolytes.

(2) Combination due to the saturation of secondary affinity only, which gives molecular compounds (polymerisation, etc.).

(3) Combination due to the saturation of both primary and secondary affinities, which gives non-polar compounds, such as methane and carbon tetrachloride.

Positive and negative affinity are defined as the tendency to lose or gain electrons. Secondary affinity is that which is developed when the primary affinity has come into play. The above three categories only represent extreme types, and most compounds take up intermediate positions between the three extremes.

[10] S. H. C. Briggs, *T.*, 1917, **111**, 253; *A.*, ii, 254.

Colloids.

Reference was made in last year's Report to a very interesting experimental method of determining the condition in which water exists in certain inorganic hydrogels, more particularly precipitated silica, alumina, and ferric hydroxide.[11] The water exists in one of three conditions, namely, free, combined, or capillary water. The method employed is to cool the gel under light petroleum in a dilatometer and to observe the volume changes as the temperature is lowered. As was pointed out, the free water freezes sharply at $-6°$, whilst the capillary water slowly freezes as the temperature falls, and the combined water, of course, is without effect. If the free and capillary water can be determined and the total water content is known, the combined water can at once be found by difference. Some further most interesting results[12] have been published which merit a description in some detail, the object of the extended observations being the more accurate determination of the combined water in the three hydrogels mentioned. The general method of investigation is simple. In the case of free water only, such as is realised by wet sand, the dilatometer readings show a steady diminution in volume as the temperature falls to $-6°$, when there is a sudden expansion due to the freezing of the water. Further cooling causes a contraction, which is a linear function of the temperature. If the dilatometer is now again allowed slowly to return to the ordinary temperature, the original readings are recovered. That is to say, the cooling and heating curves are identical at $-6°$ and below. On the other hand, if capillary water is present, this is not frozen at $-6°$, but gradually freezes as the temperature is reduced. The result is that the cooling curve below $-6°$ is not a straight line, but is concave to the temperature axis. It is possible to recognise the point at which the capillary water is all frozen by the cooling curve becoming a straight line. If the whole of the capillary water is frozen by cooling at $-78°$ and the temperature of the dilatometer then allowed slowly to rise, the first portion of the heating curve is linear. If this straight portion be extrapolated up to the temperature of $-6°$, the amount of capillary water is estimated from the difference between this extrapolated line and the cooling curve at $-6°$. The free water is calculated from the expansion originally observed at $-6°$.

Three samples of precipitated aluminium hydroxide were used,

[11] H. W. Foote and B. Saxton, *J. Amer. Chem. Soc.*, 1916, **38**, 588; *A.*, 1916, ii, 230.

[12] *Ibid.*, 1917, **39**, 1103; *A.*, ii, 364.

one which had been digested with a large excess of water for twenty four hours at 100°, whilst the other two had not been so heated, and differed merely in the length of time they had been kept. The first sample was exposed to the air until it was only slightly moist, and was then found to contain no capillary water and 36 per cent. of combined water. The other two samples contained a little capillary water and 37·8 per cent. of combined water. The compound $Al(OH)_3$ requires 34·6 per cent. of water, and the excess of combined water must be in solid solution.

The case of ferric hydroxide is more complex, for in general there is some uncertainty due to the presence of capillary water, which freezes only at very low temperatures. The combined water, found after heating the hydroxide with water at 100° for twenty-four hours, corresponds with the empirical formula $Fe_2O_3,2{\cdot}4H_2O$. After three days' heating, the combined water fell to the amount corresponding with the empirical formula $Fe_2O_3,0{\cdot}53H_2O$. After twelve days' heating, it was necessary to add a few drops of ammonia, so as to coagulate the gel, which then had the formula $Fe_2O_3,1{\cdot}04H_2O$. In this case, the reprecipitation undoubtedly increased the combined water, which happens to be close to one molecule. Evidently the combined water is slowly given off, when the precipitate is heated with water, with no tendency towards simple ratios between oxide and water. It is difficult to avoid the conviction that no well-defined compound of precipitated ferric oxide and water exists containing more than 0·5 mol. of water. When once dehydrated to this composition, the material shows no tendency to take up water. The evidence all points to a combination between ferric oxide and water in indefinite proportions, which is essentially a case of solid solution.

The results with silicic acid which has not been heated give fairly constant figures, the combined water amounting to a little more than 30 per cent. (approximately $SiO_2,1{\cdot}5H_2O$). On digesting with water at 100°, the amount of combined water decreases until, after seven days, it reaches 23 per cent. (SiO_2,H_2O). Again the results point to indefinite combination, that is to say, solid solution.

A number of papers have appeared describing the preparation of inorganic colloids, and of these a few present considerable interest. One of these contains an extension of the nucleus method for the preparation of hydrosols, more particularly those of gold.[13] Solutions of colloidal gold, which are very uniform in size of their particles, may be obtained by the use of solutions containing gold nuclei, prepared by the reduction of slightly alkaline solutions of

[13] R. Zsigmondy, *Zeitsch. anorg. Chem.*, 1917, **99**, 105; *A.*, ii, 364.

gold with phosphorus. These nuclei grow by deposition, and the number of particles is determined by the quantity of the nuclear solution used. The spontaneous formation of nuclei may be suppressed, without hindering the growth, by the addition of ammonia, potassium ferrocyanide, or potassium ferricyanide, whilst the growth may be diminished, without appreciably altering the formation of nuclei, by the addition of alkali haloids, hydrogen sulphide, or colloidal sulphur. A second method of procedure is to use a solution in which the growth is so rapid that the supply of gold is exhausted before the spontaneous formation of nuclei has become appreciable. Using water which has been distilled from potassium permanganate with a gold condenser, and adding the nuclear solution to the gold chloride before adding the hydroxylamine hydrochloride, with or without alkali carbonate, very clear, deep red solutions are obtained in which the number of particles is strictly proportional to the volume of the nuclear solution used. Blue solutions are obtained when a larger quantity of alkali is used. Similar results are obtained with hydrazine, the addition of alkali being then unnecessary. These results have independently been confirmed.[14]

Some work[15, 16] has been carried out recently on the oxidation reactions with solutions of potassium dichromate and potassium permanganate in the absence of acid. The reactions studied are those between stannous chloride and potassium dichromate, ferrous sulphate and potassium dichromate, ferrous sulphate and potassium permanganate, ferrous chloride and potassium permanganate, and in general the stoicheiometric relationships are the same as those obtained in the presence of acid. When potassium dichromate is added in the theoretical quantity to a solution of stannous chloride in the absence of acid, brown and greenish-blue gelatinous masses are formed, which dissolve to form a clear, deep olive-green solution when the whole of the potassium dichromate has been added. These solutions, which appear red by transmitted light, contain potassium and chromium chlorides, together with colloidal solutions of hydrated stannic and chromic hydroxides. On dialysis, a clear solution of the approximate composition

$$Cr_2O_3,6SnO_2$$

is obtained, and this sol contains the whole of the tin and about one-half of the chromium used in the reaction.

In the oxidation of ferrous chloride by potassium permanganate

[14] J. Reitstötter, *Koll. Chem. Beihefte*, 1917, **9**, 221; *A.*, ii, 481.

[15] M. Neidle and J. C. Witt, *J. Amer. Chem. Soc.*, 1915, **37**, 2360; *A.*, 1915, ii, 780; *ibid.*, 1916, **38**, 47; *A.*, 1916, ii, 256.

[16] M. Neidle and J. N. Crombie, *ibid.*, 1916, **38**, 2607; *A.*, ii, 93.

the collateral oxidation of the chloride ion is practically avoided by adding the permanganate gradually and stirring the solution vigorously. The products of the reaction are the chlorides of manganese, potassium, and ferric iron, together with colloidal hydrated ferric oxide. When ferrous sulphate is substituted for the ferrous chloride, the corresponding sulphates are formed and also hydrated ferric oxide, which is precipitated by the sulphate ion. One gram-equivalent of potassium permanganate, dissolved in about 600 c.c. of water, was slowly added to one gram-equivalent of ferrous chloride, dissolved in about 1 litre of water, and the resulting clear, deep brownish-red solution diluted to 2 litres. This solution remained perfectly clear for several weeks, then gradually became more and more turbid, until finally a suspension separated. Until this stage is reached dialysis yields a perfectly clear, brownish-red hydrosol of hydrated ferric oxide. After the suspension has settled, dialysis gives a hydrated ferric oxide hydrosol, which is slightly turbid in reflected light, but perfectly clear in transmitted light. The turbidity which appears on standing is due to the hydrolysis of the ferric chloride. The ferric ion protects the colloid against precipitation by the manganese and potassium chlorides. Hydrolysis of the ferric chloride decreases the concentration of the ferric ion, and, when this is reduced below the value necessary for protection, the colloid coagulates. This coagulation is, however, reversible, for the turbid mixture on dialysis yields a sol that is practically clear.

Methods have been described for the rapid preparation of the hydrosols of ferric, aluminium, and chromic hydroxides by dialysis at 75—80.[17] The solution in a beaker is kept at the required temperature by a small flame, and a parchment bag is suspended in the hot liquid. This bag is made by tying the membrane to the flanged end of a glass tube, and a current of water through this bag is maintained continuously. A general method for the preparation of the sols is to dissolve the freshly precipitated hydrated oxide in a solution of the chloride and to dialyse this mixture. In the case of aluminium and chromium hydroxides the solutions may be dialysed at once when hot, but, if it be desired to prepare the clear, brownish-red sol of hydrated ferric oxide, the solution must first be dialysed in the cold until no more iron passes through the membrane. The temperature may then be raised to 80° or even to the boiling point without affecting the nature of the colloid. If the solution is heated at the commencement of dialysis the yellow ochre variety of colloidal ferric oxide will be formed. It is found more convenient in preparing the solution to add ammonia to the

[17] M. Neidle and J. Barab, *J. Amer. Chem. Soc.*, 1917, **39**, 71; *A.*, ii, 262.

chlorides in insufficient amount to form a permanent precipitate of the hydroxide. In this way better yields of the colloids are obtained and their solutions are clearer.

It was found that colloidal chromic and aluminium hydroxides pass through the membrane to a certain extent, so that the yield is considerably smaller than theory would predict. The actual yields obtained were: $Fe(OH)_3$, 89·9 per cent.; $Cr(OH)_3$, 53·3 per cent.; $Al(OH)_3$, 41·3 per cent. As regards the time taken in the preparation of these sols by dialysis of hot solutions, it was shown, for example, that the purity of the chromic hydroxide sol obtained by dialysis of the boiling solutions in ten hours is greater than that obtained by dialysing a similar solution for seventy-three days at the ordinary temperature.

Iridium hydrosols[18] can be prepared by reduction of alkaline iridium solutions with hydrogen, hydrazine hydrate, sodium formate, or formaldehyde in presence of sodium protalbate or lysalbate as protected colloid. A clear solution of iridium chloride obtained by the addition of hydrogen chloride is added to a solution of the protective colloid when rust-brown or olive-green precipitates of the protalbate or lysalbate are produced, the colour being dependent, apparently, on the amount of free hydrochloric acid. These precipitates dissolve in sodium carbonate or hydroxide to form the blood-red hydrosols of iridium trihydroxide. With an excess of sodium hydroxide the sol becomes oxidised on exposure to air, giving the blue hydrosol of iridium tetrahydroxide. If the sol with sodium lysalbate as protective colloid is acidified, some of the lysalbic acid is left in solution and the gel is thereby enriched in iridium. By redissolving this in sodium hydroxide and repeating the process a few times, a sol may be obtained which, on drying, contains as much as 73 per cent. of iridium.

Group I.

An interesting series of papers has been published on the titration of the phosphoric acids and the constitution of the alkali metal phosphates.[19] It is well known that the neutral point obtained in titrating phosphoric acid with alkali differs with the indicator used, it being believed that sodium dihydrogen phosphate is neutral to methyl-orange and that disodium hydrogen phosphate is neutral to phenolphthalein. It is found, however, if the titration is carried out at the ordinary temperature, that this is far from correct. On the other hand, the values obtained in the titration vary considerably with the temperature, and it is shown that at a temperature

[18] C. Paal, *Ber.*, 1917, **50**, 722; *A.*, ii, 375.

[19] J. H. Smith, *J. Soc. Chem. Ind.*, 1917, **36**, 415; *A.*, ii, 309.

of 55° the neutral points observed agree very closely with the quantitative formation of the two salts, sodium dihydrogen phosphate and disodium hydrogen phosphate. A method of volumetric analysis was devised, by means of which it is possible to calculate the percentages of practically all the phosphoric acids and their salts, that may exist together in a compound, including the carbonates and the free alkali that may be present with them. The application of this method to the analysis of ordinary commercial phosphates has led to an investigation of the alkali metal phosphates. A specimen of ordinary sodium phosphate was found to contain $Na_2HPO_4 = 38{\cdot}02$, $Na_3PO_4 = 2{\cdot}41$, $H_2O = 59{\cdot}57$, whilst theory requires $Na_2HPO_4 = 39{\cdot}64$ per cent. Some clear crystals of trisodium phosphate contained $Na_3PO_4 = 41{\cdot}90$, $Na_2O = 2{\cdot}01$, $Na_2CO_3 = 0{\cdot}66$, $H_2O = 55{\cdot}43$, whilst theory requires $Na_3PO_4 = 43{\cdot}13$, $H_2O = 56{\cdot}87$ per cent.

It might be assumed that in preparing disodium hydrogen phosphate, if the theoretical amount of orthophosphoric acid and sodium hydroxide were brought together in solution, there would be no difficulty in obtaining the pure crystallised salt. This was found, however, not to be the case, and crystallisation can only be induced by the addition of a few crystals of the commercial salt. An analysis of the product showed that it has a molecular composition of $93{\cdot}93Na_2HPO_4, 6{\cdot}07Na_3PO_4$.. In the second preparation when the crystals were dried at 110°, the composition was

$$94{\cdot}5Na_2HPO_4, 5{\cdot}5Na_3PO_4.$$

Commercial disodium hydrogen phosphate has a similar composition which approximates to $17Na_2HPO_4, Na_3PO_4$. Crystals can also be obtained with a greater proportion of Na_3PO_4, and the following have been identified: $8Na_2HPO_4, Na_3PO_4$;

$$6Na_2HPO_4, Na_3PO_4;$$

$3Na_2HPO_4, Na_3PO_4$; $3Na_2HPO_4, 2Na_3PO_4$.

In the case of sodium dihydrogen phosphate, it is possible to prepare this salt in a pure state by bringing together the theoretical amounts of orthophosphoric acid and sodium hydroxide and by concentration of the resulting solution.

Difficulties were also found in the preparation of trisodium phosphate. On bringing together the theoretical proportions of acid and alkali hydroxde, followed by considerable concentration, crystals are obtained having a constitution $Na_2HPO_4, 2Na_3PO_4$. The mother liquor, on further concentration, gave crystals of the composition $18Na_3PO_4, Na_2O$, the water content in each case not being determined. By using a slight excess of sodium hydroxide over the amount required by theory, the crystals which first separate have the composition $17{\cdot}5Na_3PO_4, Na_2O$, and it is believed that the

correct molecular composition of this salt is represented by $18Na_3PO_4,Na_2O$.

A new phosphate of sodium, $Na_4P_6O_{17}$, is also described, containing a much higher proportion of acid oxide than is represented by sodium dihydrogen phosphate or metaphosphate. The new salt is readily prepared in an impure state by evaporating mixtures of sodium hydroxide or carbonate with phosphoric acid in sufficient excess, and igniting the residue. Any excess of the acid is volatilised during the ignition, so that the proportion of acid is the highest with which sodium oxide is capable of combining to form a salt stable at a red heat. The salt forms a fused, glassy mass, which dissolves slowly in cold and more readily in warm water. The solution is nearly neutral to both methyl-orange and phenolphthalein. On prolonged boiling with water, it is converted into sodium metaphosphate and free orthophosphoric acid. In the presence of free mineral acid sodium orthophosphate is formed.

A remarkable property of this salt, to which the name of sodium polyphosphate is given, is its exceedingly energetic corrosive action on glass, porcelain, and even platinum and silica vessels. This action is, naturally, most pronounced at the high temperature of fusion, when the glaze of porcelain vessels is readily attacked. Silica vessels are also sensibly attacked, and silica enters into the composition of the resultant salt. A platinum vessel was strongly attacked, becoming brittle in the places where it had been in contact with the fused salt. In the case of a nickel vessel the residue consisted entirely of a mixture of sodium and nickel pyrophosphates. This corrosive action renders it almost impossible to prepare the salt in a pure condition.

Some further work may be noted on silver peroxynitrate,[20] which has been the subject of very many investigations in the past. When an aqueous solution of silver nitrate is electrolysed between insoluble electrodes, silver is deposited at the cathode and silver peroxynitrate at the anode, there being presumably a simultaneous formation of nitric acid. Both deposits are crystalline, and they grow rapidly towards one another in arborescent crystals. The anode crystals soon become detached, and they are then attacked by the free nitric acid and pass into solution with the liberation of gas. The composition of these crystals is doubtful, many views having been expressed. Experiments are now described in which the electrolyte is kept in continuous circulation, and the decomposing action of the nitric acid is avoided by means of suspended silver carbonate. Two strengths of solution were used, namely, one containing 5 per cent. and the other 20 per cent. of silver

[20] M. J. Brown, *J. Physical Chem.*, 1916, **20**, 680; *A.*, ii, 88.

nitrate. The percentage of silver in the compound varies from 79·03 to 79·82, and the coulometer ratio of the compound to copper deposited in the same circuit varies from 2·98 to 2·69, but there is apparently no relation between the fluctuations in the coulometer ratio and the silver content. The compound cannot be a pure oxide, because the oxides up to Ag_2O_3 have too high a silver content, and Ag_2O_3 has far too low a coulometer ratio; neither can it be a hydrated oxide of definite composition. The determinations agree with the formula $2Ag_3O_4,AgNO_3$, which requires 79·9 per cent. for the silver content and 2·97 for the coulometer ratio. The small differences between the calculated and observed values are probably due to secondary disturbances.

In the rhythmical precipitation of silver chromate by means of ammonium dichromate the small crystals of ammonium nitrate, which also separate rhythmically, are coloured by silver chromate, being yellowish-green to red, according to the concentration.[21] Similar coloured crystals are obtained when a solution of ammonium nitrate containing a little ammonium dichromate is mixed with a drop of silver nitrate and allowed to evaporate on a glass slide. Both silver chromate and dichromate can take small quantities of ammonium or potassium nitrate into solid solution. The colour of pure silver chromate is always greenish-black, and the red substance usually supposed to be a separate modification is a mixture of silver chromate and the solid solutions with the nitrates.

Certain double fluorides of rubidium and cæsium with the metals of the fourth group have been prepared and examined.[22] The general method is to add the alkali carbonate to a solution of the quadrivalent metal oxide in hydrogen fluoride, but in the case of lead the solution of the acetate in hydrogen fluoride was used. The resulting solutions give characteristic crystals of the double salts on being allowed to remain. The following salts are described: Rb_2SnF_6, Cs_2SnF_6, Rb_2PbF_6, Cs_2PbF_6, Rb_2GeF_6, and Cs_2GeF_6.

Potassium stannichloride can conveniently be prepared by the oxidation of the stannochloride by means of chlorine.[23] A concentrated solution of the salts in the molecular proportion of two parts of potassium chloride and one part of stannous chloride is prepared with the addition of a few drops of concentrated hydrochloric acid. A slow stream of chlorine is passed in for about three hours, when the solution is treated with a little concentrated hydrochloric acid and slowly evaporated at 50—70° for about two hours. After some time crystals of the stannichloride separate out. The method was

[21] F. Köhler, *Zeitsch. anorg. Chem.*, 1916, **96**, 207; *A.*, ii, 32.
[22] A. Skrabal and J. Gruber, *Monatsh.*, 1917, **38**, 19; *A.*, ii, 263.
[23] J. G. F. Druce, *T.*, 1917, **111**, 416; *A.*, ii, 309.

tested with mixtures of potassium chloride and manganese chloride and of potassium chloride and lead chloride, but without success.

Group II.

The melting point of glucinum has been determined and found to be $1278° \pm 5°$.[24] The element, prepared electrolytically from sodium glucinum fluoride, was pressed into pastilles and fused in a magnesia tube in hydrogen. The product contained 99·5 per cent. of glucinum, the principal impurity being the carbide. The melting point was found from the heating and cooling curves. An approximate determination of the heat of fusion gave 277 cal. per gram.

The literature contains many references to the preparation and properties of zinc peroxide and its hydrates, and some further work is to be added to the list.[25] The addition of a solution of zinc sulphate to excess of a solution of sodium hydroxide containing hydrogen peroxide gives a quantitative precipitation of the zinc as hydroperoxide. A more convenient method was found to be as follows. Freshly ignited pure zinc oxide was left for several hours with the calculated quantity of 30 per cent. hydrogen peroxide solution at $-10°$. A product was obtained which above 2° formed a pasty mass, and when dried on a porous plate at 35—40° over soda-lime was obtained as a white powder. It contained 8·04 per cent. of active oxygen and corresponded almost exactly with the composition $2ZnO,H_2O_2$ or $Zn_2O\begin{matrix}O\cdot OH\\OH\end{matrix}$. Towards water, alcohol, or ether at the ordinary temperature it is quite stable, and is only slowly decomposed by 2*N*-sodium hydroxide. It does not appear, however, to be a simple chemical individual, since by trituration with water it can be separated into fractions containing varying quantities of active oxygen. Similar products are obtained by boiling zinc carbonate with excess of 30 per cent. hydrogen peroxide solution.

It is concluded that zinc perhydrate generally consists of a mixture of substances derived from $Zn(OH)_2$ and $O(ZnOH)_2$, the hydroperoxides being of the types $OH\cdot Zn\cdot O\cdot OH$ and

$$Zn(OH)\cdot O\cdot Zn\cdot O\cdot OH.$$

By a study of the equilibrium relations in the ternary system formed by the alkaline earth metal haloids, the corresponding hydroxides, and water, certain basic haloid salts of these metals have been investigated.[26] The basic salt, $CaI_2,3CaO,16H_2O$, is stable in

[24] G. Oesterheld, *Zeitsch. anorg. Chem.*, 1916, **97**, 1 ; *A.*, ii, 89.
[25] F. W. Sjöström, *ibid.*, 1917, **100**, 237 ; *A.*, ii, 533.
[26] J. Millikan, *Zeitsch. physikal. Chem.*, 1917, **92**, 59 ; *A.*, ii, 257.

contact with solutions containing from 28·44 to 66·68 per cent. of calcium iodide. The only basic chloride of strontium has the composition $SrCl_2,SrO,9H_2O$, and this only exists in contact with solution at temperatures above 20·5°. Strontium bromide and strontium iodide respectively form the two basic salts, $SrBr_2,SrO,9H_2O$ and $SrI_2,2SrO,9H_2O$.

The basic phosphates of calcium have also been studied by a similar method, this work being the fourth contribution to our knowledge of the calcium phosphates by the same author.[27] The present investigation deals with the region lying between those which are characterised by the existence of dicalcium hydrogen phosphate and calcium hydroxide as stable solid phases, and the observations were made at 25°, 100°, and 170—200°. Two, and only two, phosphates of calcium more basic than dicalcium phosphate exist, which can be in stable equilibrium with an aqueous solution at 25° and, probably, at any temperature. These are tricalcium phosphate, $Ca_3P_2O_8$, and hydroxyapatite,

$$(Ca_3P_2O_8)_3,Ca(OH)_2.$$

There is no evidence for the existence of phosphates between dicalcium hydrogen phosphate and tricalcium phosphate, or of the formation of solid solutions.[28, 29] Hydroxyapatite is the only stable solid phase over a range of acidity of great practical importance, as it can exist in contact with faintly acid, neutral, or alkaline solutions. It is probable that this compound is the only calcium phosphate that can permanently exist under normal soil conditions. The importance of hydroxyapatite is obvious in relation to the nature of bone phosphate, and this is considered to be a mixture of hydroxyapatite and calcium carbonate with small amounts of adsorbed bicarbonates of sodium, potassium, and magnesium.

A study has also been made of the ternary system $CuSO_4$–CuO–H_2O with the object of ascertaining the cause of the varying composition of the mineral brochantite.[30] Series of observations were made at 25°, 37·5°, and 50°, and it was found that in all probability the solid basic substances obtained are not definite compounds, but are rather to be regarded as a three-component system in which all three components ($CuSO_4$, CuO, H_2O) are continuously variable within certain limits. The maximum number of molecules of CuO that can be taken up by one molecule of $CuSO_4$ is two, and the formula for the most basic salt is probably $CuSO_4,2CuO,2H_2O$.

[27] H. Bassett, jun., *Zeitsch. anorg. Chem.*, 1907, **53**, 34, 49; 1908, **59**, 1; *A.*, 1908, ii, 675; *T.*, 1917, **111**, 620; *A.*, ii, 413.

[28] F. K. Cameron and A. Seidell, *J. Amer. Chem. Soc.*, 1905, **27**, 1503; *A.*, 1906, ii, 163.

[29] F. K. Cameron and J. M. Bell, *ibid.*, 1512; *A.*, 1906, ii, 164.

[30] S. W. Young and A. E. Stearn, *ibid.*, 1916, **38**, 1947; *A.*, 1916, ii, 621.

In general, the experiments indicate the existence of a series of metastable sulphates, and go to show that it is to be expected that brochantite would evidence variable composition according to the conditions of its formation.

Cadmium nitrite[31] has been prepared by trituration of pure recrystallised cadmium chloride and silver nitrate in a mortar, water being added from time to time until the filtrate gave no indication of excess of either of the parent substances. On evaporation in a vacuum over sulphuric acid, bright pale yellow crystals were obtained with the composition $Cd(NO_2)_2$. On heating, this salt begins to decompose slowly at 150°. As nitric oxide is the chief gaseous product, the main portion of the salt evidently decomposes according to the equation $3Cd(NO_2)_2 = 2CdO + Cd(NO_3)_2 + 4NO$, since the brown residue was found to be cadmium nitrate mixed with cadmium oxide. A parallel decomposition also takes place according to the equation $Cd(NO_2)_2 = CdO + NO + NO_2$. The solution obtained by the interaction of zinc sulphate and barium nitrite evolves nitric oxide when concentrated by evaporation, and the residue consists of basic zinc nitrate.

The compound, glucinum metavanadate,[32] $Gl(VO_3)_2,4H_2O$, has been prepared by boiling equimolecular solutions of glucinum hydroxide and vanadium pentoxide with water for about one hour, after which the solution was filtered and concentrated. This, while hot, was poured into a large volume of 95 per cent. alcohol, when a copious deposit of yellow particles was produced, which in twenty-four hours had settled to a voluminous layer of yellow crystals. The salt is sparingly soluble in cold water, but readily so in hot water. It is practically insoluble in chloroform, ether, or absolute alcohol, but is soluble in pyridine to about the same extent as in water. The crystals lose the whole of their water of crystallisation over sulphuric acid.

Group III.

An alkaline solution of gallium hydroxide in sodium hydroxide, on electrolysis at the ordinary temperature, usually deposits gallium as liquid globules on the cathode. It is found, however, that such a solution, after separation of the indium, on electrolysis at 0°, deposits the metal in black, arborescent forms.[33] These gallium trees are hard and are permanent so long as they are kept at a temperature 10° below the melting point. Although black

[31] P. C. Rây, *T.*, 1917, **111**, 159; *A.*, ii, 208.

[32] P. H. M. P. Brinton, *J. Amer. Chem. Soc.*, 1916, **38**, 2361; *A.*, ii, 32.

[33] H. S. Uhler and P. E. Browning, *Amer. J. Sci.*, 1916, [iv], **42**, 389; *A.*, ii, 34.

in external appearance, they present, when cut, the usual silvery lustre of pure gallium. When placed in water, gas is slowly evolved, and the metal becomes coated with black, grey, and white patches. A specimen of electrolytic gallium containing a trace of zinc was purified by heating the metal in a current of dry hydrogen at a dull red heat, when the whole of the zinc sublimed.

The separation of gallium from indium may be effected (i) by solution of gallium hydroxide from the mixed hydroxides by sodium hydroxide, (ii) by crystallisation of the ammonium alums from 70 per cent. alcohol, and (iii) by crystallisation of the cæsium alums. A gallium preparation containing 10 per cent. of indium, with traces of zinc, copper, and lead, was practically pure after ten crystallisations of the cæsium alums.

A continuation of the investigation of the action of acids on aluminium may be noted.[34] The previous experiments[35] dealt with nitric acid, and the new investigation deals with acetic acid at varying concentrations and temperatures. The aluminium, containing Al = 99·1, Si = 0·45, Fe = 0·45 per cent., was used in the form of thin, rolled strips, which were generally annealed before use. The surface of the metal was cleaned with sodium hydroxide and washed with dilute nitric acid before each experiment.

In the case of boiling dilute acid, the rate of dissolution rises continuously until the concentration of the acid falls to 1 per cent. The dissolution is greatly affected by the products of the interaction, the disturbance growing very rapidly with increasing dilution. A definite reason cannot yet be assigned, but it has been found that acid which has become highly active can be distilled without losing its activity. Solutions of acid which have been boiled in contact with aluminium become turbid after a period, and the nature of the turbid solutions varies in the different cases. With acids of concentration between 60 and 5 per cent., the turbidity appears to be due to the separation of basic acetate or acetates of aluminium. In the case of acids of about 0·2 per cent. concentration, the turbidity may be due to the formation of a colloidal solution of aluminium hydroxide. Solutions containing between 5 and 0·2 per cent. of acetic acid yield turbid solutions of an intermediate character.

Except in the case of the anhydrous acid, aluminium is uniformly attacked by boiling acetic acid at all concentrations, no evidence of local action having been observed.

In general, aluminium is only slowly attacked by cold acetic acid, the rate of dissolution increasing with increasing dilution of

[34] R. Seligman and P. Williams, *J. Soc. Chem. Ind.*, 1917, **36**, 409; *A.*, ii, 317.

[35] *Ibid.*, 1916, **35**, 665; *A.*, ii, 435.

the acid, the highest rate so far observed occurring with an acid containing 0·02 per cent. acetic acid. The rate is frequently high at first, but rapidly falls, and then remains constant over long periods. In most cases the attack is uniform, but local action has been observed at concentrations between 70 and 95 per cent., and in cases in which the metal has been allowed to remain in contact with thin films of dilute acid, which have thereby become subjected to extensive aeration.

The action of boiling acetic acid (about 10 per cent.) on aluminium is practically unaffected by the addition of up to 1 per cent. of sodium chloride, potassium bromide, iodide, or nitrate, whereas an equivalent amount of sodium sulphate raises the rate of dissolution appreciably. With the cold acid, on the other hand, the rate of dissolution is increased tenfold by 1 per cent of sodium chloride, whereas potassium bromide affects a smaller increase, and potassium iodide and nitrate are without action; 0·5 per cent. of sodium sulphate causes a fourfold increase in the rate of dissolution. The most serious effect of the addition of substances was noted in the case of the boiling 80 per cent. acid. Here the rate of dissolution is raised by 1 per cent. of sodium chloride from 290 to 16,000, by 1 per cent. of potassium bromide the rate is only increased from 290 to 485, whilst potassium iodide and potassium nitrate are practically without effect. Sulphuric acid (0·5 per cent.) in the form of sodium sulphate somewhat increases the rate of dissolution.

In the Report for 1912, reference was made to the existence of borohydrates which possess very interesting properties.[36] Some further work has been carried out on these substances and may briefly be described, especially as some of the original conclusions have been modified.[37] The new experiments show that when a mixture of 2·25 parts of magnesium powder and 1 part of anhydrous boric acid is heated in a current of hydrogen until the reaction is complete, solutions are obtained by treatment of the product with water which are free from boric acid and magnesium borate, and contain only substances which are described as borohydrates. The main product of the action of water is an insoluble compound of magnesium oxide with a borohydrate, reaction taking place in accordance with the equation

$$Mg_3B_2 + 6H_2O = Mg_3B_2(OH)_6 + 3H_2.$$

The soluble borohydrates and gaseous compounds of boron and

[36] M. W. Travers and R. C. Rey, *Proc. Roy. Soc.*, 1912; [A.], **87**, 163; *A.*, 1912, ii, 938.

[37] M. W. Travers, N. M. Gupta, and R. C. Rey, Pamphlet, 1916, p. 46; *A.*, ii, 307.

hydrogen, which are also formed, are attributed to secondary reactions.

The solutions of borohydrates are unstable, but the stability is increased in presence of traces of ammonia. On the addition of acids to the solutions, hydrogen is evolved, and the acid solutions decolorise iodine Analyses and molecular weight determinations indicate that the mean composition of the borohydrates is represented by $H_6B_2O_2$. When the solutions are evaporated to dryness and the residue heated, a mixture of the oxide, B_2O_2, with magnesium oxide is obtained.

If the mixture of magnesium boride and boric acid is insufficiently heated, or if excess of boric acid is employed in preparing the mixture, the solutions obtained by the action of water differ from those described above in that they contain magnesium borate and boric acid, as well as one or more borohydrates.

When magnesium boride, after prolonged treatment with water, is acted on by strong ammonia, a solution is obtained which does not lose hydrogen when kept in an exhausted tube and does not oxidise in contact with the air. On addition of acids to this solution, hydrogen is rapidly evolved, and the acid solution reacts with iodine. When the solution is evaporated to dryness at low temperature in a vacuum, a white, crystalline residue remains, which gives off hydrogen when heated and is transformed into the oxide, B_4O_5. This oxide dissolved in water with the formation of a yellow solution, which rapidly absorbs oxygen in contact with the air, the reaction being represented by the equation

$$2B_4O_5 + O_2 + 12H_2O = 8B(OH)_3.$$

Molecular weight determinations of the substance in the ammoniacal solution prepared as described above seem to show that the compound has the formula $H_{12}B_4O_6,2NH_3$. When ammoniacal solutions of the borohydrates are evaporated to dryness and treated with water, a small quantity of insoluble residue is left, which appears to be a hydrated derivative of an oxide containing less oxygen than those previously referred to.

In discussing the above results, the work of Stock and his pupils may be recalled on the hydrides of boron obtained by the action of acid on magnesium boride. This work was described at some length in the Reports for 1912, 1913, 1914, and 1915.

Group IV.

An improvement in the method of the preparation of carbon suboxide has enabled this gas to be prepared in large quantities, with the result that the physical constants have been determined

with greater accuracy than has previously been possible.[38] The poor yields usually obtained by the action of phosphoric oxide on malonic acid are largely due to the polymerisation of the suboxide under the catalytic action of the phosphoric oxide. If the suboxide is removed rapidly by carrying out the reaction in a good vacuum and condensing the product by means of liquid air, a volume of the gas corresponding with as much as 25 per cent. of the malonic acid can be obtained The melting point of carbon suboxide is $-111{\cdot}3°$ and its boiling point 6°, and the vapour pressure at 0° is 587—589 mm. The gas is very readily soluble in carbon disulphide or xylene. It is interesting to note that the polymerisation of the gas to the red substance, which is soluble in water, is catalysed remarkably by the polymeride itself. The gas may sometimes be kept for days, but as soon as polymerisation sets in, it completely disappears within a day. In contact with phosphoric oxide, the gas polymerises within a fraction of a minute.

Carbonyl sulphide[39] can be prepared by the action of hydrochloric acid on commercial ammonium thiocarbamate, according to the equation $NH_2{\cdot}CO{\cdot}S{\cdot}NH_4 + 2HCl = COS + 2NH_4Cl$. The gas is purified by being bubbled through a 33 per cent. solution of sodium hydroxide, which absorbs carbon dioxide and hydrogen sulphide, after which it is dried by means of calcium chloride and phosphoric oxide; it is then condensed by means of liquid air, and finally fractionated. The gas is fairly readily soluble in weaker solutions of alkali hydroxide, but only slowly dissolves in a 33 per cent. solution. It is odourless and is slowly decomposed by water, but in the dry state it is permanent even in sunlight. One part of water dissolves 0·54 vol. at 20°, and one part of alcohol and one part of toluene at 22° dissolve 8 vols. and 15 vols. respectively. It has D^{-87} 1·24, m p. $-138{\cdot}2°$, b. p. $-50{\cdot}2°/760$ mm.

A considerable amount of work has been done on zirconium dioxide and zirconium salts. The possibility of the use of the dioxide as the basis of glazes for metal ware and of scientific apparatus has long been recognised. As regards its use in making apparatus, difficulties have been found in that cracks readily develop in the finished articles. If, however, the dioxide is first melted at a very high temperature and the solidified fusion finely ground, the powder so obtained can be used for making apparatus similar to porcelain ware, for the apparatus is perfectly sound and does not develop cracks. The melting point of pure zirconium dioxide is about 3000°.[40]

[38] A. Stock and H. Stoltzenberg, *Ber.*, 1917, **50**, 498 ; *A.*, ii, 308.
[39] A. Stock and E. Kuss, *ibid.*, 159 ; *A.*, ii, 205.
[40] E. Podszus, *Zeitsch. angew. Chem.*, 1917, **30**, i, 17 ; *A.*, ii, 480.

Other experiments have been made on the fusibility of mixtures of zirconia with other oxides.[41] Zirconia containing 98·73 per cent. of ZrO_2, the remainder being SiO_2 and Fe_2O_3, melts at 2563±10°. Glucina, alumina, yttria, and thoria are suitable for addition to zirconia, causing little volatilisation at high temperatures, whilst magnesia causes fuming and silica lowers the melting point excessively. For the preparation of crucibles, the addition of 1 per cent. of alumina is recommended for use at 2000°, 1 per cent. of thoria for use at 2200°, and from 1 to 3 per cent. of yttria for use at 2400°. The addition of larger quantities increases the porosity and has no advantage.

It appears that the hydrate of zirconium fluoride does not possess the usually assigned composition $ZrF_4,3H_2O$, but is really a hydrate of acid zirconyl fluoride, $ZrOF_2,2HF,2H_2O$.[42] The arguments are based on the fact that this compound at 140° in dry air loses 2 mols of water, giving the anhydrous acid fluoride, which when heated above 140° in air loses 2 mols. of hydrogen fluoride, giving zirconyl fluoride, $ZrOF_2$. This compound when cold reabsorbs 2 mols. of hydrogen fluoride. The anhydrous normal zirconyl fluoride may also be obtained by crystallising the hydrated acid fluoride from dilute aqueous solution and drying the product, $ZrOF_2,2H_2O$, at 120°. If the anhydrous or hydrated acid fluoride is heated at 200° in an atmosphere of hydrogen fluoride, zirconium fluoride is obtained which, in the cold, absorbs hydrogen fluoride, probably to form fluozirconic acid, H_2ZrF_6.

Somewhat analogous relationships are exhibited between the bromides of zirconium. By the evaporation of a solution of zirconium hydroxide in hydrobromic acd on a water-bath, the hydrate of zirconyl bromide, $ZrOBr_2,8H_2O$, is obtained. This compound, when dried in a vacuum or in a current of dry air, gives the hydrate, $ZrOBr_2,3{\cdot}5H_2O$, which is stable up to 60—70°. Above this temperature, it loses both water and hydrobromic acid, giving the compound $ZrOBr_2,ZrO_2$. This basic bromide is also slowly deposited from an $N/100$-solution of zirconyl bromide on long keeping. By the addition of ether to an alcoholic solution of zirconyl bromide, the compound, $ZrOBr_2,ZrO_2,2H_2O$, is obtained. In a current of hydrogen bromide at a red heat, the basic bromide is converted into zirconium bromide, $ZrBr_4$.

By mixing varying molecular proportions of zirconium oxide and sulphuric acid and drying the products at 200°, a series of sub-

[41] O. Ruff and G. Lauschke, *Zeitsch. anorg. Chem.*, 1916, **97**, 731; *A.*, ii, 95.

[42] E. Chauvenet, *Compt. rend.*, 1917, **164**, 630, 727, 816, 864, 946; *A.*, ii, 264, 321, 322, 374.

stances has been obtained the composition of which, by the method of densities, appears to be $Zr(SO_4)_2$, $Zr(SO_4)_2,ZrO_2$, $5Zr(SO_4)_2,7ZrO_2$, $3Zr(SO_4)_2,5ZrO_2$, $Zr(SO_4)_2,2ZrO_2$, $Zr(SO_4)_2,3ZrO_2$. It would seem more probable, however, that these are in reality zirconyl sulphates.

A new class of basic salts of zirconium has also been described.[43] A basic sulphate of this element, of indefinite composition, is prepared by partly neutralising an impure dilute solution of zirconium sulphate in sulphuric acid with ammonia This basic sulphate is readily decomposed by aqueous ammonia in the cold, giving a hydroxide readily soluble in acids. By the crystallisation of its solution in hydrochloric acid, an oxychloride is formed, which is not a uniform substance. By recrystallisation of this oxychloride from hydrochloric acid, it is separated into two salts, the normal oxychloride, $ZrOCl_2,2H_2O$, and the new compound, $Zr_5O_8Cl_4,22H_2O$. This new oxychloride is a crystalline salt, very readily soluble in water, and can be recrystallised unchanged from hydrochloric acid solution.

Soluble sulphates precipitate from solutions of 5 : 4-basic zirconium chloride an insoluble sulphate, $Zr_5O_8(SO_4)_2,xH_2O$, where x is probably 14. This is a non-crystalline compound, soluble in concentrated sulphuric acid. Corresponding with the 5 : 4-chloride and the 5 : 2-sulphate is a hydroxide prepared from either of these by the action of ammonia. It is distinct from normal zirconium hydroxide, since, when redissolved in hydrochloric acid, it forms the 5 : 4-basic chloride. From analogy, its composition is given as $Zr_5O_8(OH)_4$. It is suggested that the new salts have structural formulæ of the type $Zr(O{\cdot}ZrO{\cdot}Cl)_4$, which would account for their remarkable stability. A basic sulphate is also described, produced by the addition of sulphuric acid to a boiling solution of zirconium oxychloride, $ZrOCl_2,8H_2O$. This appears to have the same composition as the 5 : 2-sulphate, although it is otherwise distinct therefrom. Evidence was also obtained of yet another oxychloride of zirconium.

The very remarkable analogy between the above new salts of zirconium and those of tin has not been commented on by the author. It may be pointed out that there is a basic chloride of tin, prepared from metastannic acid, $H_5Sn_5O_{15}$, which has the composition $Sn_5O_8Cl_4,7H_2O$, and is clearly the analogue of the new zirconium oxychloride. At the same time, the β-stannic hydroxides and chlorides do not appear properly to have been systematised. Metastannic acid is usually considered to have the composition $H_2Sn_5O_{11},4H_2O$, owing to the fact that the metastannates

[43] E. H. Rodd, *T.*, 1917, **111**, 396 ; *A.*, ii, 322.

have the composition $M'_2Sn_5O_{11},4H_2O$. This form gives rise to the oxychloride $Sn_5O_9Cl_2,4H_2O$ (metastannyl chloride). On the other hand, the oxychloride $Sn_5O_8Cl_4,7H_2O$ must be derived from a metastannic acid of the composition $H_4Sn_5O_{12},3H_2O$, and this would be the analogue of the new zirconium hydroxide. Judging from analogy, therefore, it would seem that the conclusion that the new zirconium hydroxide has the composition $H_4Zr_5O_{12}$ is fully justified, although perhaps it may be combined with three molecules of water.

Again, by boiling metastannic acid with water, parastannic acid is obtained, and the composition of this is usually represented as $H_2Sn_5O_{11},2H_2O$, since it gives an oxychloride with the composition $Sn_5O_9Cl_2,2H_2O$. The ratio between tin and chlorine is the same as in metastannyl chloride, but the properties of the two oxychlorides are different. The suggestion may be made, therefore, that the second new basic zirconyl sulphate is related to the first in exactly the same way as parastannyl chloride is related to metastannyl chloride.

Group V.

A method is described for the preparation of pure bismuth from the commercially pure metal.[44] The nitrate, if already of fair purity, is dissolved in half its weight of 8 per cent. nitric acid and mixed with an equal weight of the concentrated acid. The crystals, which separate on cooling to 0° or −10°, are washed with a little ice-cold nitric acid. All impurities are thus concentrated in the mother liquor. The nitrate is converted into the oxide by heat, and the oxide is then reduced by fusion with potassium cyanide. A further purification, if necessary, is effected by melting the metal under paraffin and removing the first (purest) crystals by means of a glass spoon. Purified bismuth melts at 271·0°, and when pressed into wire at 195° has a specific electrical resistance of 1·20.

Some experiments with nitrogen trichloride may be noted, together with some investigations of the reactions between chlorine and ammonia.[45, 46] The nitrogen trichloride was prepared by the Hentschel method,[47] using, however, carbon tetrachloride as the solvent in place of benzene. The solution of the trichloride in carbon tetrachloride may be preserved for several weeks in the dark

[44] F. Mylius and E. Groschuff, *Zeitsch. anorg. Chem.*, 1916, **96**, 237; *A.*, ii, 37.

[45] C. T. Dowell and W. C. Bray, *J. Amer. Chem. Soc.*, 1917, **39**, 896; *A.*, i, 306.

[46] W. C. Bray and C. T. Dowell, *ibid.*, 1917, **39**, 905; *A.*, ii, 307.

[47] W. Hentschel, *Ber.*, 1897, **30**, 1792; *A.*, 1897, ii, 447.

before they become greatly contaminated with chlorine from the decomposition of the trichloride. Only one reducing agent was found, namely, sodium sulphite, which reduces nitrogen trichloride quantitatively to ammonia; this reaction occurs in accordance with the equation $3Na_2SO_3 + NCl_3 + 3H_2O = 3Na_2SO_4 + 2HCl + NH_4Cl$. In the case of the other reducing agents investigated, some nitrogen is evolved in a secondary reaction. These were ferrous sulphate, arsenious acid, sodium arsenite, hydrogen sulphide, and potassium iodide in acid solution. Iodine reacts with nitrogen trichloride, setting free nitrogen and forming chlorides of iodine; on the addition of water to the resulting solution, iodic acid is precipitated. Sodium hydroxide reacts with nitrogen trichloride, giving a rapid evolution of nitrogen, but the reaction is not quantitative, since some ammonia is also formed.

Quinol is converted into hexachloroquinol, whilst carbamide in acid solution is not acted on, but in neutral solution there is a slow evolution of nitrogen. Nitrogen trichloride reacts slowly with dilute ammonium chloride solution and more rapidly with a concentrated solution to give nitrogen and hydrogen chloride, $NH_4Cl + NCl_3 = N_2 + 4HCl$.

The reactions have been considered which occur when ammonia and chlorine react in acid solution, in alkaline solution, and in dilute solutions of ammonia and hypochlorous acid. It has been shown previously [48] that, when chlorine gas reacts with 0·5 per cent. ammonia solution, the reaction takes place in accordance with the equation $3NH_3 + 6Cl_2 = N_2 + NCl_3 + 9HCl$, equimolecular quantities of nitrogen and nitrogen trichloride being produced. This reaction, which is of the ninth order, has been criticised, and as a result of a number of experiments it is concluded that the reaction is only the resultant of a number of intermediate reactions, the first of which is the formation of monochloroamine, according to the equation $NH_3 + Cl_2 = HCl + NH_2Cl$.

Solutions of nitrous acid may be prepared far more readily by the interaction between equivalent quantities of barium nitrite and sulphuric acid than by the action of hydrochloric acid on silver nitrite.[49] In the latter case the reaction rarely passes to completion owing to the coating of the silver nitrite with the insoluble silver chloride. Measurements of the velocity of decomposition of nitrous acid were made at 0°, 21°, and 40°, and they show that the reaction is unimolecular. The velocity-coefficients at these three temperatures are 0·00014, 0·00022, and 0·00057 respectively. Ac-

[48] W. A. Noyes and A. C. Lyon, *J. Amer. Chem. Soc.*, 1901, **23**, 460; *A.*, 1901, ii, 601.

[49] P. C. Rây, M. L. Dey, and J. C. Ghosh, *T.*, 1917, **111**, 413; *A.*, ii, 301.

cording to conductivity determinations, the dissociation constant of nitrous acid at 0° is $6{\cdot}0 \times 10^{-4}$. The most concentrated solution of the acid that can be obtained at 0° by the above method is 0·185*N*.

An investigation has been made of the reduction of vanadic acid by hydriodic acid.[50] Several papers have been published in which this reaction has been discussed, and very contradictory results have been obtained. Amongst the most recent work may be mentioned that of Ditz and Bardach, who stated that the product of the reaction is vanadium trioxide.[51] This conclusion is at variance with the results of previous workers, and in consequence the present investigation was undertaken. It was found that the reaction is influenced very considerably by the oxidation of the hydrogen iodide by means of air, and care was therefore taken to exclude air by means of a current of hydrogen. The iodine set free in the reaction was removed by means of carbon disulphide, the addition and removal of carbon disulphide being continued until no further iodine was extracted after several hours' keeping. The combined carbon disulphide solutions were then titrated with sodium thiosulphate solution. It was concluded from the results obtained that the reduction only proceeds to quadrivalent vanadium; further, the reduced vanadium solution is blue, and not green, as it ought to be if a tervalent vanadium compound be present.

It would seem probable that the oxidation of hydrogen iodide by air is catalysed by vanadium pentoxide.

Reference may be made to the preparation of certain double salts of bismuth chloride with chlorides of bivalent metals.[52] The bismuth chloride is dissolved in the smallest possible quantity of concentrated hydrochloric acid, and the solution is treated with the carbonate or hydroxide, or in a few cases the chloride of the bivalent metal. The latter was added in some cases so long as it dissolved, in other cases in amounts less than this. In no case did the solution of bismuth chloride (1 mol.) dissolve more than 1 mol. of the bivalent chloride. The solutions are then concentrated over sulphuric acid until the double salts crystallise. These double salts are colourless (except when a coloured cation has been added), hygroscopic, and are decomposed by water, bismuth oxychloride being precipitated. Three series of salts have been obtained. The first series may be regarded as the derivatives of pentachlorobismuthic acid, H_2BiCl_5, and of these are described

[50] G. Edgar, *J. Amer. Chem. Soc.*, 1916, **38**, 2369; *A.*, ii, 36.

[51] H. Ditz and F. Bardach, *Zeitsch. anorg. Chem.*, 1915, **93**, 97; *A.*, 1916, ii, 347.

[52] R. F. Weinland, A. Alber, and J. Schweiger, *Arch. Pharm.*, 1916, **254**, 521; *A.*, ii, 374.

$BiCl_3,MgCl_2,8H_2O$; $BiCl_3,CaCl_2,7H_2O$; $BiCl_3,SrCl_2,8H_2O$; $BiCl_3,BaCl_2,4H_2O$; $BiCl_3,CoCl_2,6H_2O$; $BiCl_3,NiCl_2,6H_2O$. The second series may be looked upon as the derivatives of tetrachlorobismuthic acid, $HBiCl_4$, and is exemplified by $2BiCl_3,CaCl_2,7H_2O$; $2BiCl_3,SrCl_2,7H_2O$; $2BiCl_3,BaCl_2,5H_2O$. The third series contains derivatives of heptachlorodibismuthic acid, HBi_2Cl_7, and is exemplified by $4BiCl_3,MgCl_2,16H_2O$; $4BiCl_3,SrCl_2,12H_2O$; $4BiCl_3,MnCl_2,12H_2O$; $4BiCl_3,FeCl_2,12H_2O$; $4BiCl_3,CoCl_2,12H_2O$; $4BiCl_3,NiCl_2,12H_2O$.

Group VI.

The behaviour of "potassium ozonate" on keeping, and on treatment with water or dilute acids, has been discussed.[53] This compound loses its colour on keeping and changes into potassium hydroxide, oxygen, and potassium tetroxide. Since potassium tetroxide, on treatment with water, yields oxygen and hydrogen peroxide, it may be written as $K{\cdot}O{\cdot}O{\cdot}K,O_2$, and, therefore, the reactions of the ozonate, to which may be ascribed the composition $(KOH)_2O_2$, may be expressed as follows: $3[(KOH)_2O_2] = 2K_2O_2,O_2 + 2KOH + 2H_2O$, $2[(KOH)_2O_2] = 2K_2O_2 + 2H_2O + O_2$, and $K_2O_2 + (KOH)_2O_2 = K_2O_2,O_2 + 2KOH$. It is supposed that ozone decomposes into oxygen and atomic oxygen in contact with the alkali, and that it is only the latter which reacts. This would account for the fact that no more powerful oxidising agent is obtained.

Rubidium and cæsium hydroxide form orange-red "ozonates," and cæsium carbonate also becomes temporarily orange-coloured in a current of ozone.

When a current of ozonised oxygen[54] is passed through acetic acid, acetic anhydride, ethyl acetate, chloroform, or carbon tetrachloride at the ordinary temperature a blue solution is obtained, the colour persisting for more than fifteen to twenty hours with the two last-named solvents, but disappearing more rapidly with the others. Comparative experiments with a current of oxygen containing approximately 6 per cent. of ozone indicated that carbon tetrachloride dissolves seven times as much ozone as an equal volume of water, and, when saturated, contains three times as much ozone as the original ozonised oxygen.

The reactions of ozone with iodine, iodides, iodates, and periodates have been investigated.[55] Ozone reacts with solutions of

[53] W. Traube, *Ber.*, 1916, **49**, 1670; *A.*, 1916, ii, 613.

[54] F. Fischer and H. Tropsch, *ibid.*, 1917, **50**, 765; *A.*, ii, 463.

[55] E. H. Riesenfeld and F. Bencker, *Zeitsch. anorg. Chem.*, 1916, **98**, 167; *A.*, ii, 201.

potassium iodide instantaneously, even below 0°, but the final equilibrium in the solution between $K^{\cdot}$, OH', I', IO', IO_3', and IO_4' is only attained after some days. The higher the concentration of the ozone in the oxygen used the greater is the influence of the hydroxyl ions. In acid solutions the ordinary reaction is accompanied by one in which three atoms of oxygen from a molecule of ozone take part. This may consist of an addition of ozone to iodine ions, forming iodate ions, or of a formation of hydrogen peroxide. Ozone is without action on neutral and acid solutions of potassium iodate, but in alkaline solution oxidation to periodate takes place. Ozone has no action on periodates .No evidence was found for the existence of a modification of oxygen containing more than three atoms, the differences observed by Harries between the results of gravimetric and volumetric estimations being due to the action of hydroxyl ions. This conclusion, however, is not accepted by Harries.[56]

The preparation of certain new salts of bivalent chromium, together with the properties of chromous salts, may be noted. Chromic salts may be electrolytically reduced to chromous salts with a cathode of pure lead.[57] This reduction has been studied quantitatively by measuring the amount of chromous salt produced at any moment by adding excess of iodine and titrating the unused portion, and also by following the course of the reduction by readings at a voltameter and at the electrolytic cell of the volume of hydrogen liberated in a given time. To protect the solutions against the air they are covered with light petroleum. The most favourable conditions are the electrolysis of the violet chromic salts in moderately acid concentrated solutions with a current density of 2·5 amperes per sq. dcm. The more common green salts in equivalent solutions require a greater expenditure of current than the violet salts, but they yield much more concentrated solutions. They are, therefore, more suitable in the end for the production, at any rate, of solutions rich in chromous salts, but not entirely free from chromic salts. The same slower reduction of the green complexes is observed when the solutions are treated with zinc.

By mixing a well-cooled, concentrated solution of chromous chloride with various alkali salts of organic acids, the following new salts have been obtained[58]: chromous formate,

$$Cr(HCO_2)_2,2H_2O,$$

red cubes; chromous ammonium formate, $NH_4Cr(HCO_2)_3$, pale brownish-red needles; red chromous glycollate, $Cr(C_2H_3O_3)_2$; Bordeaux-red chromous malonate, $CrC_3H_2O_4$; blue chromous sodium

[56] C. Harries, *Zeitsch. anorg. Chem.*, 1917, **99**, 196; *A.*, ii, 464.

[57] W. Traube and (Miss) A. Goodson, *Ber.*, 1916, **49**, 1679; *A.*, 1916, ii, 625.

[58] W. Traube and W. Passarge, *ibid.*, 1962; *A.*, 1916, ii, 626.

malonate, $Na_2Cr(C_3H_2O_4)_2$. The solutions of all these salts have the usual blue colour of chromous salts.

Chromous salts are gradually oxidised, especially in acid solutions, with the liberation of hydrogen, thus: $2CrO + H_2O = Cr_2O_3 + H_2$, and for this reason they are able in the presence of water to reduce compounds with double or triple linkings. Acetylene is reduced to ethylene, but not to ethane. For example, on shaking 1200 c.c. of this gas with a solution of chromous chloride, made by adding an excess of zinc to 70 grams of green chromic chloride dissolved in 120 c.c. of 25 per cent. hydrochloric acid, complete reduction occurred in less than an hour. Nitrous oxide in the presence of alkali hydroxide is reduced quantitatively to nitrogen; similarly, nitric acid and hydroxylamine are reduced quantitatively to ammonia. The yield of ammonia obtained, however, by the reduction of nitrous acid is not quantitative.

Although chromium phosphate has formed the subject of a number of investigations during the past sixty years, many of its properties appear to have been unrecorded. Some new investigations on this salt may be noted.[59] When cold solutions of equal weights of chrome alum and disodium hydrogen phosphate are mixed, a violet precipitate of amorphous chromic phosphate is produced. This precipitate, when allowed to remain in the solution for a day or two, is converted into a violet, crystalline hexahydrate. It is essential that the first amorphous precipitate be not left too long in contact with the solution, as after a week it becomes entirely convered into a green, amorphous tetrahydrate. This change is catalysed by sodium sulphate solution or chrome alum solution, the latter being the more powerful catalyst, and is greatly influenced by temperature.

If the violet hexahydrate is heated at 100° for some time, or, better, if boiled with water for half an hour, it is completely converted into a green, crystalline hydrate, $CrPO_4,4H_2O$. On boiling the violet, crystalline hexahydrate with acetic anhydride, it forms a green, crystalline dihydrate similar in appearance to the tetrahydrate. Both these green hydrates are stable in the presence of moist air or water. When heated to low redness they quickly become converted into a fine, black, amorphous chromic phosphate, and when strongly heated this changes into a green basic salt. Amorphous, green chromium phosphate is prepared by precipitating a hot chrome alum solution with excess of disodium hydrogen phosphate, and washing repeatedly with boiling water. In a desiccator at the ordinary temperature this compound rapidly loses weight until the composition is $CrPO_4,4H_2O$. When heated at 60°

[59] A. F. Joseph and W. N. Rae, *T.*, 1917, **111**, 196; *A.*, ii, 210.

it loses two molecules of water, and at dull red heat it is converted into brown, amorphous chromic phosphate.

By the interaction[60] of chromyl chloride and phosphorus trichloride or phosphorus tribromide in dry carbon tetrachloride solution, precipitates are obtained which, when collected, washed with carbon tetrachloride, and dried in a current of dry, CO_2-free air, have the composition $CrOCl,POCl_3$ and $CrOBr,POBr_3$ respectively. The reaction being extremely violent, it is carried out in 0·2 mol. solutions, and takes place according to the equation $2CrO_2Cl_2 + PCl_3 = 2(CrOCl,POCl_3) + PCl_5$. These double compounds are extremely deliquescent and react with water with development of heat, according to the equation $CrOCl,POCl_3 + 2H_2O = CrCl_3 + HCl + H_3PO_4$. On ignition, the compounds CrOCl (or $Cr_2O_3,CrCl_3$) and CrOBr (or $Cr_2O_3,CrBr_3$) are obtained.

Molybdenum pentasulphide, Mo_2S_5, has been prepared by reducing a solution of ammonium molybdate, containing more than 20 per cent. of sulphuric acid, with zinc, until the colour is dark red, and then diluting, filtering, and saturating the solution with hydrogen sulphide.[61] The precipitate is collected and washed with hot water and then with alcohol. It is shaken repeatedly with carbon disulphide, washed with ether, and dried at 68—75°, when it has the composition $Mo_2S_5,3H_2O$. One molecule of water is lost at 135—140°, but further heating causes decomposition. Careful heating in carbon dioxide gives the anhydrous sulphide, Mo_2S_5, which is almost black. When the hydrated compound is heated in hydrogen sulphide the compound, $2Mo_2S_5,3H_2S$, is formed.

Group VII.

The mechanism of the conversion of alkaline solutions of sodium hypochlorite into sodium chlorate has been studied.[62] At a temperature of 50° the reaction is of the second order rather than of the third, and, therefore, the first stage is represented by the equation $2NaClO = NaClO_2 + NaCl$. There is also an evolution of oxygen, which evidently occurs according to the equation $2NaClO = O_2 + 2NaCl$. Further, the transformation of the chlorite into chlorate is a bimolecular reaction, and follows the equation $NaClO + NaClO_2 = NaClO_3 + NaCl$. The formation, therefore, of chlorate from hypochlorite occurs according to the equations (1) $2NaClO = NaClO_2 + NaCl$, and (2) $NaClO + NaClO_2 = NaClO_3 + NaCl$. The

[60] H. S. Fry and J. L. Donnelly, *J. Amer. Chem. Soc.*, 1916, **38**, 1923; *A.*, 1916, ii, 626.

[61] F. Mawrov and M. Nikolov, *Zeitsch. anorg. Chem.*, 1916, **95**, 188; *A.*, ii, 479.

[62] F. Foerster and P. Dolch, *Zeitsch. Elektrochem*, 1917, **23**, 137; *A.*, ii, 367.

latter reaction proceeds much more rapidly than the former. The following velocity constants have been obtained: K_1, $50° = 0{\cdot}0019$, $25° = 0{\cdot}00010$; K_2, $50° = 0{\cdot}050$, $25° = 0{\cdot}0035$. The temperature-coefficient of K_1 is 3·15, whilst that of K_2 is 2·88.

Group VIII.

There is considerable uncertainty regarding the existence of ferric trisulphide, Fe_2S_3, and some light has been thrown on the matter by further work. When moist ferric hydroxide, or ferric hydroxide suspended in water, is treated with hydrogen sulphide, it becomes black, owing to the formation of ferric trisulphide, in accordance with the equation $2Fe(OH)_3 + 3H_2 = Fe_2S_3 + 3H_2O$.[63] In a moist condition in the absence of air, or in the presence of excess of hydrogen sulphide, it is transformed into a mixture of the disulphide and sulphide, thus: $Fe_2S_3 = FeS_2 + FeS$. This change takes about a week at the ordinary temperature, but only a few hours at 60°. The mixture produced, being only partly soluble in dilute hydrochloric acid, may easily be distinguished from the original trisulphide, which is readily and completely soluble. When dried in a vacuum over phosphoric oxide, ferric trisulphide is very stable.

When exposed to the action of the air in presence of alkali, ferric trisulphide gradually becomes pale yellow, sulphur being deposited. The product resembles limonite in appearance, and when dried gives a fine, yellow powder containing a constant percentage of water, which is less than that corresponding with $Fe(OH)_3$.

When precipitated ferrous sulphide is boiled with flowers of sulphur, iron disulphide is formed. Ferric disulphide is also precipitated when a solution of sodium trisulphide is added slowly to a boiling solution of ferrous sulphate, sulphur being liberated at the same time.

Since ferric disulphide is the final product of the action of hydrogen sulphide on ferric hydroxide in the absence of alkali, the production of iron pyrites in nature can be explained.

A very convenient method has been described for the preparation of chloroplatinic acid, which obviates all difficulties arising from the formation of nitrosoplatinic chloride and chloroplatinous acid, the removal of which is so troublesome when aqua regia is used.[64] The method consists in the use of hydrogen peroxide, which

[63] V. Rodt, *Zeitsch. angew. Chem.*, 1916, **29**, i, 422; *A.*, ii, 142.

[64] P. Rudnick and R. E. Cooke, *J. Amer. Chem. Soc.*, 1917, **39**, 633; *A.*, ii, 264.

readily effects the dissolution of platinum black in hydrochloric acid, yielding a solution which is at once free from nitrosoplatinic chloride and entirely oxidised to chloroplatinic acid. The method may be described in detail, and consists in covering 10 grams of platinum black, dried, but not ignited, with 50 c.c. of hydrochloric acid. The mixture is heated to 50—60°, and hydrogen peroxide (3 –30 per cent.) is slowly added at such a rate as to maintain a moderate evolution of chlorine. When the platinum has entirely been dissolved, the solution is concentrated. When a 3 per cent. solution of hydrogen peroxide is used, it may be necessary to evaporate the solution to a smaller bulk in order to effect the complete dissolution of the platinum.

Reference may be made to some work on the oxides of ruthenium, rhodium, and osmium. Finely powdered ruthenium oxidises rapidly when heated in oxygen, the maximum of absorption of oxygen corresponding very closely with the oxide, RuO_2.[65] The value is, however, slightly lower, owing to volatilisation. It is independent of the temperature between 700° and 1000°, although the rate of formation of ruthenium dioxide varies considerably. The formation of the volatile tetroxide begins at 600° and increases rapidly with the temperature, being 4000 times as great at 1200° as at 700°. The sublimate of tetroxide, however, contains crystals of the dioxide.

On the other hand, when rhodium is heated in air or oxygen at temperatures from 600° to 1000°, the greyish-black oxide, Rh_2O_3, is always formed, the rate of formation increasing rapidly with the temperature.[66] At 1150°, the oxide is completely decomposed, the metal being obtained.

Colloidal solutions of osmium dioxide are obtained by the reduction of the alkali osmates with alcohol or by the hydrolysis of the osmichlorides.[67] The reactions are as follows:

$$K_2OsO_4 + 2H_2O + C_2H_5{\cdot}OH = OsO_2,2H_2O + 2KOH + C_2H_4O;$$
$$K_2OsCl_6 + 4H_2O = OsO_2,2H_2O + 2KCl + 4HCl.$$

By the addition of electrolytes to the neutral solutions, the dioxide can be precipitated, but it forms a colloidal solution again when treated with acids, alkali hydroxides, or ammonia, or washed free from electrolytes. Concentrated solutions of the colloidal oxide appear black by reflected light or blue by transmitted light.

The oxide prepared by reduction or by the hydrolysis of

[65] A. Gutbier, G. A. Leuchs, H. Wiessmann, and O. Maisch, *Zeitsch. anorg. Chem.*, 1916, **96**, 182; *A.*, ii, 38.

[66] A. Gutbier, A. Hüttlinger, and O. Maisch, *ibid.*, **95**, 225; *A.*, ii, 483.

[67] O. Ruff and H. Rathsburg, *Ber.*, 1917, **50**, 484; *A.*, ii, 323.

ammonium osmichloride retains alkalis and organic substances very firmly. As the result, the dry powder may kindle on exposure to the air or detonate on warming. An old preparation or one that has been warmed with water for some time is not so dangerous, but it then contains much metallic osmium.

Amorphous osmium dioxide, containing about 1 per cent. of sodium chloride, is obtained on heating potassium osmichloride with pure sodium hydroxide solution in the absence of air. The dried powder has the composition $OsO_2,2H_2O$. It loses one molecule of water at 100° and the other at 200°, the residue being a bluish-black powder. This oxide reacts with hydrogen with almost explosive violence, and with oxygen readily to give osmium tetroxide. When heated in an indifferent atmosphere, it becomes dark brown, and decomposes at about 500° into osmium and osmium tetroxide. The reaction is reversible, as the pure dioxide can be obtained by heating very finely divided osmium with osmium tetroxide at 650° in an atmosphere of nitrogen. When the dioxide is heated in an atmosphere of osmium tetroxide (partial pressure about 100 mm.) at 640°, it changes into a crystalline form. A copper-coloured sublimate is usually deposited, and it is possible that the volatile oxide to which this sublimed dioxide is due is a trioxide, thus: $OsO_2 + OsO_4 = 2OsO_3$.

E. C. C. Baly.

ORGANIC CHEMISTRY.

Part I.—Aliphatic Division.

During the greater part of the period embraced by the current review, the writer had the feeling that if the Annual Report was to preserve its reputation for being a fair index of contemporary research, the section on aliphatic compounds would on this occasion be brief, disconnected, and even uninteresting. The publications which appeared during the second half of the year did much to modify this first impression, but it has been a case of making the best of things, and the Report is thus presented with a full knowledge of many shortcomings. The task of following and studying the course of organic research during the past twelve months has certainly afforded many compensations to the writer, and to institute comparisons between recent work and the product of more peaceful days would be unfair to those who have kept formal research alive despite the distractions of the times. In any case, such criticism as might be called for does not apply to our own Journal, the pages of which are unsullied by those records of meaningless compound-making so prominent in other periodicals to which good taste prevents more pointed reference. There has been no sacrifice of standard in order to preserve bulk, and there has been in many cases a gratifying combination of experiment and speculation, so that, taking everything into account, there is reason to be moderately satisfied with a year's steady if unexhilarating progress.

Hydrocarbons.

In collecting the material for this section of the Report, the writer anticipated a difficulty which has not been forthcoming. In few classes of compounds more than in the aliphatic hydrocarbons did it seem probable that care would be necessary to restrict selection to topics of general theoretical importance, and leave more technical subjects to the Reports on Applied Chemistry.

No such critical selection has, however, been necessary, as the number of publications on aliphatic hydrocarbons has been small,

and in only a limited number of cases do they admit of synopsis or brief discussion. For the time being, systematic research on simple representatives seems to be at a standstill.

As has recently been the case, a number of papers have appeared dealing with the conversion of paraffins into aromatic hydrocarbons, and the impression has gradually been gained that the actual results obtained must give greater promise of ultimate technical adoption than the published descriptions would lead one to expect. As a general rule, the conversion from the paraffinic to the aromatic type is effected by "cracking," and a prominent feature of recent work in this field is the steady rise in the pressures and a corresponding diminution in the temperatures employed.[1, 2] Incidentally, it may be remarked that somewhat similar considerations apply to the degradation of aromatic hydrocarbons[3] in the absence of catalysts.

Unsaturated compounds still continue to demand most attention in this section, and the synthetical applications of acetylene, to which reference has repeatedly been made in recent Reports, may well revolutionise many methods of preparation in the near future. Under this heading, few new results have been forthcoming in the past year, and published references to acetylene have been disappointing. In a somewhat different field, attempts have been continued to trace the part played by acetylene in the formation of heterocyclic[4] compounds, and although numerous aromatic products have been obtained by subjecting the hydrocarbon to the action of hydrogen sulphide, ammonia, or steam at high temperatures, the work leaves the impression of being in some degree empirical.

Greater interest will be taken in the suggestion[5] that copper acetylide plays a definite part, when used as a catalyst for the conversion of benzenediazonium chloride into chlorobenzene, in contributing its carbon atoms to the final product. The idea originally put forward by Sandmeyer, that the catalysis is in the first place due to the formation of copper chloride, does not take into account the destiny of the acetylene thus liberated, but, as a result of the study of secondary reactions, it is now maintained that such is the case.

[1] G. Egloff and T. J. Twomey, *Met. Chem. Eng.*, 1916, **15**, 245; *A.*, 1916, i, 786.

[2] W. F. Rittman, *Brit. Pat.*, 9163 of 1915; *A.*, i, 14.

[3] Synthetic Hydro-Carbon Co., *Fr. Pat.*, 479786; *A.*, i, 15.

[4] R. Meyer and H. Wesche, *Ber.*, 1917, **50**, 422; *A.*, i, 313.

[5] V. V. Scharvin and N. I. Plachuta, *J. Russ. Phys. Chem. Soc.*, 1916, **48**, 253; *A.*, i, 179.

Researches on the polymerisation of olefinic hydrocarbons have been continued on normal lines and have given results which are consistent with earlier observations,[6] but there is a marked falling-off in papers dealing with caoutchouc. In last year's Report, considerable space was devoted to the discussion of several papers on this subject by Ostromisslenski, and further contributions from the same worker are now available. His views as to structure and isomerism of caoutchoucs have been slightly simplified, but he continues to apply the expressions "normal" and "abnormal" to these compounds according to the physical properties of the complexes, and without reference to the chemical behaviour of the ozonides prepared from them. Descriptions are now given[7] of the caoutchoucs obtained by polymerising various hydrocarbons, or mixtures of hydrocarbons, which agree fairly well with the observations of earlier workers, and several conflicting results, which have been the cause of much discussion in the past, are now explained. He points out that although the polymerised product from pure isoprene is naturally different from that obtained from the isoprene–amylene mixture, it is impossible to detect even considerable proportions of the amylene constituent by analysis, and maintains that variation in physical property alone gives any index of composition. Another point of interest is the conversion of the isoprene–amylene caoutchouc obtained by the sodium method into an isomeric β-form by the action of either barium peroxide or benzoyl peroxide. It would appear, so far as any generalisations can be established in these reactions, that the use of peroxides as polymerising reagents generally gives a different product from that formed by the action of sodium. An exception is, however, furnished by the case of erythrene caoutchouc, of which one variety is produced, irrespective of the reagent employed in its formation.

In a further paper,[8] the same author furnishes some results which are more attractive to the organic chemist. Accepting that the polymerisation of vinyl bromide gives rise to the symmetrical bromide of erythrene caoutchouc, he has attempted to correlate the corresponding chloride of the complex with polymerised vinyl chloride. The latter compound in the liquid condition is rapidly transformed under the influence of light from a mercury lamp into α-caouprene chloride. This particular variety is soluble, and thus the molecular weight could be determined, giving a result

[6] S. V. Lebedev and A. A. Ivanov, *J. Russ. Phys. Chem. Soc.*, 1916, **48**, 997; *A.*, i, 126.

[7] I. I. Ostromisslenski, *ibid.*, 1071; *A.*, i, 399.

[8] I. I. Ostromisslenski, *ibid.*, 1916, **46**, 1132; *A.*, i, 404.

in close agreement with the formula $C_{32}H_{48}Cl_{16}$. Apparently the compound is saturated, and it is thus regarded as a single ring structure containing the fragment $-CHCl\cdot CH_2-$ repeated sixteen times. So far, the results described are convincing, but the evidence on which the statement is made that the chloro-compound is identical with the symmetrical chloride of erythrene caoutchouc could only be valuated by those who have personal experience in this type of work. What is claimed to be the unsymmetrical chloride of erythrene caoutchouc has also been prepared directly from the hydrocarbon complex by treatment, in carbon tetrachloride solution, with the appropriate amount of chlorine similarly dissolved. On the evidence produced, however, it is difficult to draw any real distinction between this product and caouprene chloride.

It is evident that Ostromisslenski brings to the caoutchouc problem both fresh ideas and new working methods, but, for the time being, he has this field of research to himself.

Alcohols and their Derivatives.

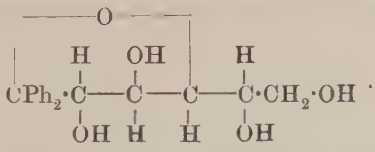
Very little work has recently appeared dealing with unsubstituted alcohols, and attention may be restricted to one or two investigations which deal with structural problems in the polyhydroxy-series. Since the appearance of Böeseken's papers on the conductivity changes which ensue when boric acid is added to solutions of polyhydroxy-compounds, much interest has been displayed in the application of his principles to questions of constitution. According to Böeseken, the reaction between the acid and the alcohol is limited to cases where hydroxyl groups are favourably situated, and a positive result is indicated by a marked exaltation in conductivity and also, in the case of optically active compounds, of the rotatory power. These views have in recent years been supported in a number of ways, and a further step has now been made by the preparation of definite compounds of mannitol and dulcitol with metallic metaborates.[9]

It is true that the isolation of such compounds has only an indirect bearing on Böeseken's views, but, in some particulars, the results are suggestive. Thus, in the case of mannitol, the rotatory power is but little affected when the amount of acid present is increased beyond equimolecular proportions, but this does not hold for the case of metallic borates, where apparently the reaction is independent of the configuration of the alcohol. In investigations

[9] A. Grün and H. Nossowitsch, *Monatsh.*, 1916, **37**, 409; *A.*, 1916, i, 787.

of this nature, some danger is involved in the possibility that the method of allocating hydroxyl groups to structural positions on the evidence of conductivity may be applied in cases where external factors may vitiate the result. This applies with special force to hydroxy-acids, which are profoundly affected by variations in the concentration of their solutions, and some idea of the complications thus introduced is gained from inspection of recent results obtained with pyruvic and lactic acids.[10] In any case, in work of this description, due regard must be paid to the degree of hydration attained by boron trioxide in solution, and to the possibility of organic molecular complexes being formed by combination with different boric acids.

Until recently, comparatively little use has been made of the Grignard reaction in research on polyhydroxy-compounds, but obviously this is largely explained through lack of appropriate solubilities. This difficulty may, however, be overcome by the use of soluble derivatives, from which the substituting groups can afterwards be removed, and further examples involving this modification are now forthcoming.[11] Starting from a fully acetylated gluconolactone, reaction with magnesium acyl haloids gives the corresponding sorbitol derivatives, of which αα-dibenzoylsorbitol may be quoted as an example. By a similar process, αα-dibenzoyldulcitol has been obtained from tetra-acetylgalactonolactone, and an unusual feature of the compound in question is the ease with which it is converted into the internal anhydride.



Any evidence as to the formation of definite anhydrides in this series is valuable, in view of the obscurity in which similar changes in the sugar group are enveloped, and it should be possible to establish relationships between ring-formation and configuration by further work similar to that now described.

Aldehydes and Ketones.

The steady and persistent demand for the simpler aliphatic aldehydes which has been apparent for some years has focussed

[10] J. Böeseken, L. W. Hansen, and S. H. Bertram, *Rec. trav. chim.*, 1916, **35**, 309; *A.*, 1916, ii, 209.

[11] C. Paal (with C. Küster and C. Roth), *Ber.*, 1916, **49**, 1583; *A.*, 1916, i, 787.

attention on the inadequacy of the usual oxidation methods of preparing these compounds. No doubt, so far as acetaldehyde is concerned, processes commencing from acetylene will go far to solve this difficulty, and new variations of this reaction have been described.[12] Not only the preparation, but the identification, of simple aldehydes and their isolation in a pure condition are matters of concern to those who work in this field, and thus a welcome will be accorded to a review in which the behaviour of typical members towards various reagents is summarised.[13] The results described show that lower members of the series of aliphatic aldehydes are best characterised as nitrophenylhydrazones, whilst for higher members, semicarbazone formation is more satisfactory. As has recently been the experience of workers in the sugar group, the use of diphenylmethanedimethyldihydrazine, as a reagent for the identification of aldehydes generally, has met with striking success. Before leaving this subject, it may be mentioned that the isomeric *o*-bromophenylhydrazones of glyoxylic acid have now been examined in greater detail, and the conditions governing their formation established. The reactions of the two compounds are more diagnostic than is often the case with such stereo-isomerides, and thus spatial formulæ have been ascribed to them with some degree of certainty.[14]

Although the function of formaldehyde as a methylating agent in certain cases has long been recognised and utilised in working processes, no very satisfactory explanation has been offered as to the mechanism of its action. The problem is, however, greatly simplified as the result of a study[15] of the changes in which methylamines are formed by this agency. In particular, the identification of methyl formate and carbon dioxide as significant products when ammonium chloride reacts with impure formaldehyde under mild conditions, and the successive drop in yield of these products when mono- or di-methylammonium chlorides are employed, show that, during the process, oxidation changes are operative in varying degree. The suggestion is made that the first stage of the reactions which lead to the formation of mono- and di-methylamines is the production of methyleneimine.

$$\text{I. } \text{H}\cdot\text{COH} + \text{NH}_3(\text{HCl}) \longrightarrow \text{H}\cdot\text{CH}\!<\!\begin{matrix}\text{OH}\\ \text{NH}_2\end{matrix} \longrightarrow \text{CH}_2\!:\!\text{NH}(\text{HCl}).$$

[12] Union Carbide Co., *U.S. Pats.*, 1213486 and 1213487; *A.*, i, 318.

[13] C. D. Harries, *Chem. Zentr.*, 1916, ii, 991; *A.*, i, 210.

[14] M. Busch, F. Achterfeld, and R. Seufert, *J. pr. Chem.*, 1915, [ii], **92**, 1; *A.*, i, 228.

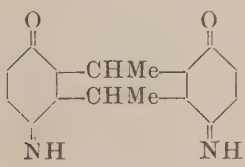
[15] E. A. Werner, *T.*, 1917, **111**, 844; *A.*, i, 632.

In the presence of formaldehyde, simultaneous oxidation and reduction then ensues, the reaction involving a molecule of water.

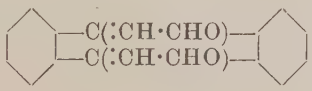
II. $CH_2{:}NH(HCl) + H_2O + H{\cdot}COH \longrightarrow CH_3{\cdot}NH_2,HCl + H{\cdot}CO_2H.$

The extension of similar principles to the interaction of formaldehyde and alkylammonium chlorides accounts for the production of dimethylamine, and indicates that the tertiary amine is not a direct product of the reaction. The paper to which reference is now made contains more than the theoretical discussion, as good working directions are given for the preparation on the large scale of methylamine and dimethylamine salts.

Now that clearer views prevail as to the nature of aldehyde-ammonia, more interest is attached to synthetical reactions involving the use of the compound, although, as a rule, its behaviour is somewhat fickle. An additional example of this is furnished[16] by the fact that, when condensed with *p*-benzoquinone, the amino-groups of the aldehyde-ammonia play a part in the reaction, as the essential product has the structure indicated by (I). On the other hand, the behaviour towards anthraquinone is entirely different, as a nitrogen-free derivative (II) is produced.



(I.)



(II.)

This variation is not entirely due to the structural difference between the quinones which take part in the reaction, and is probably attributable to the temperature conditions, as, in the one case, the aldehyde–ammonia doubtless reacted as such, and, in the other, as a mixture of free aldehyde and ammonia.

The difficulties attendant on the study of glyoxal are one by one disappearing as the result of much patient research, and there is now ample choice in the reagents by means of which the polymerised aldehyde may be converted into the monomeric form.[17] Of these, the most successful is acetic anhydride, but it is to be noted that prolonged action with this reagent results in the formation of the symmetrical tetra-acetate, $C_2H_2(OAc)_4$, which presumably has an acetal structure. The compound in question is well defined and displays so many reactions characteristic of mono-

[16] P. C. Ghosh, *T.*, 1917, **111**, 608; *A.*, 1, 517.
[17] K. Hess and C. Uibrig, *Ber.*, 1917, **50**, 365; *A.*, i, 319.

meric glyoxal that, in the future, it may play an important part in the development of this difficult subject.

A further step has also been made in a problem which has a direct bearing on the vexed question of the curious degradations which ensue when a hexose is acted on by ammonia. Some years ago, it was shown that ammoniacal zinc oxide reacts with glucose to give methylglyoxaline, and the probable course of the reaction is now indicated by the results of a further research.[18] It has been found that methylglyoxaline is formed immediately on adding ammoniacal zinc oxide to methylglyoxal and formaldehyde in aqueous solution. This at once gives a clue to the formation of methylglyoxaline from the sugars, and it is significant that, in a similar test, dihydroxyacetone reacted only slowly.

As experimental difficulties are frequently encountered in preparing cyanohydrins, a brief reference may be made to modifications of the usual procedure.[19] Of the variations suggested, the most useful is to dissolve the aldehyde in a solvent immiscible with water and shake with an aqueous solution of potassium cyanide and ammonium chloride. This particular process answers well, and its application is not restricted, as indicated in the paper, to cases where the cyanohydrin is insoluble in the extraneous solvent used.

Turning to ketones, attention should be directed to evidence[20] showing that dry acetone combines with dry calcium chloride in two proportions, as it is satisfactory to have a definite explanation of the tenacity with which the pure ketone is retained by this drying agent.

Presumably as a side issue of other work, several papers have appeared on the condensation of pyrrole with simple ketones.[21] The results described are, however, by no means simple, as in general the products, although definite and crystalline, contain four pyrrole residues united to four ketonic residues, and are thus of the same order of complexity as chlorophyll and hæmin. There is a special interest attached to sparingly soluble, stable derivatives of ketones, as their formation may possibly be elaborated into methods of estimating acetone in the presence of related substances. This possibility is supported by the fact that acetone and methyl ethyl ketone react very unequally with pyrrole,[22]

[18] B. J. Sjollema and Mlle. A. J. H. Kam, *Rec. trav. chim.*, 1916, **36**, 180; *A.*, 1916, i, 791.

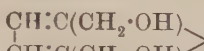
[19] A. Albert, *Ber.*, 1916, **49**, 1382; *A.*, 1916, i, 821.

[20] L. S. Bagster, *T.*, 1917, **111**, 494; *A.*, i, 493.

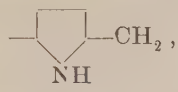
[21] V. V. Tschelincev and B. V. Tronov, *J. Russ. Phys. Chem. Soc.*, 1916, **48**, 105; *A.*, i, 91; 1916, **48**, 127; *A.*, i, 93; 1916, **48**, 1197; *A.*, i, 411.

[22] V. V. Tschelincev, B. V. Tronov, and S. G. Karmanov, *ibid.*, 1210; *A.*, i, 412.

but, on the other hand, enter into simultaneous condensation with the reagent to give a "mixed" compound of similar type. A further idea of the complexity of these reactions is given by the results obtained in the condensation of pyrrole with formaldehyde,[23] as it has been shown that the reaction can be modified so as to give various types of products. Thus, under mild conditions of alkaline condensation, 2:5-dimethylolpyrrole,



is formed, but in the presence of acids, the polymeride of



is produced in excess. Even in the absence of acids, the changes involved are obscure and give rise to substances very easily affected by polymerising reagents.

Acids and their Derivatives.

As a preliminary to more complex subjects, reference may be made to attempts to prepare simple derivatives of the common acids which may aid their identification. *p*-Nitrobenzyl bromide has been suggested as a useful reagent for this purpose, as it reacts smoothly with the alkali salts of acids, and the resulting esters are, as a rule, readily crystallised. So far as aromatic acids are concerned, the products appear to be easily characterised,[24] but, in the case of many aliphatic acids, the melting points of the esters are inconveniently low and not sufficiently far apart to be diagnostic. This may, in some measure, be compensated for by the fact that the yields are good,[25] but the process breaks down in a number of examples where characteristic tests are hard to find. On the other hand, the normal *p*-nitrobenzyl esters of malonic acid homologues are easily distinguishable, but, unfortunately, no result was obtained with lævulic or mucic acids.[26]

Numerous references in the patent literature show that the preparation of acetic acid from acetylene has been improved, so as to run as a continuous process, by the use of preformed acetic acid as a solvent. The technical preparation of acetic anhydride

[23] V. V. Tschelincev and B. V. Maksorov, *J. Russ. Phys. Chem. Soc.*, 1916, **48**, 748; *A.*, i, 164.

[24] E. Lyons and E. E. Reid, *J. Amer. Chem. Soc.*, 1917, **39**, 1727; *A.*, i, 559.

[25] E. E. Reid, *ibid.*, 124; *A.*, i, 333.

[26] J. A. Lyman and E. E. Reid, *ibid.*, 701; *A.*, i, 334.

has also been modified,[27] and simple methods are now described whereby the compound can be obtained free from chlorinated by-products, which are of frequent occurrence when sulphur chlorides are used as the anhydride-forming reagents.[28] In this and other similar cases, acetic anhydride functions as à suitable diluent, which serves to moderate the reaction and limit the formation of extraneous products.[29]

Before leaving the subject of anhydrides, mention should be made of new results obtained by the use of thionyl chloride. As is well known, the metallic salts of organic acids are acted on by thionyl chloride to give the corresponding anhydrides, but, under certain conditions, further reaction takes place and the acid chloride results. The mechanism of these changes has already been carefully investigated,[30] and the earlier views are now supported by fresh evidence.[31] Apparently thionyl chloride acts on salts in consecutive reactions as shown below:

$$\text{I.}\quad 2R\cdot CO_2M + SOCl_2 \longrightarrow (RCO_2)_2SO + 2NaCl.$$

The intermediate product, which can be regarded as a derivative of sulphurous acid, may decompose according to the scheme:

$$\text{II.}\quad (RCO_2)_2SO \longrightarrow SO_2 + (RCO_2)_2O,$$

or, in the presence of excess of thionyl chloride, in terms of the equation

$$\text{III.}\quad (RCO_2)_2SO + SOCl_2 \longrightarrow 2R\cdot COCl + 2SO_2.$$

The above explanation is founded on the behaviour of silver salts towards thionyl chloride, but it is only on rare occasions that the intermediate sulphurous ester is sufficiently stable to admit of isolation.

Another example is, however, provided when potassium xanthate is used in the reaction, which is then arrested definitely at the first stage,

$$2EtO\cdot CS\cdot SK \longrightarrow (EtO\cdot CS\cdot S)_2SO.$$

It may be remarked that when sulphur chloride is employed in the production of anhydrides, similar intermediate compounds are formed which are exceedingly well defined and comparatively stable.

Much patient research has been expended on the subject of the oxidation by hydrogen peroxide of the homologues of *iso*butyric

[27] H. Dreyfus, *Brit. Pat.*, 17920 of 1915; *A.*, i, 194.
[28] H. Dreyfus, *Brit. Pat.*, 100450 of 1916; *A.*, i, 441.
[29] H. Dreyfus, *Fr. Pat.*, 478951; *A.*, i, 2.
[30] W. S. Denham and Miss H. Woodhouse, *T.*, 1913, **103**, 1861.
[31] M. M. Richter, *Ber.*, 1916, **49**, 1026; *A.*, 1916, i, 706.

acid.[32] The results obtained are simple, inasmuch as the oxidation products are few in number, but their formation is by no means easily explained. Thus, as a rule, two ketones and one aldehyde are produced, as represented below:

$$CHMe_2\cdot[CH_2]_n\cdot[CH_2]_2\cdot CO_2H \longrightarrow \begin{cases} CHMe_2\cdot[CH_2]_n\cdot CH_2\cdot CHO \\ CHMe_2\cdot[CH_2]_n\cdot COMe \\ Me\cdot CO\cdot Me \end{cases}$$

One generalisation which has emerged from this work is that the lengthening of the chain between the carboxyl group and the tertiary carbon atom diminishes the yield of acetone, which is the predominating product from lower members of the series. In a related subject of research,[33] it is interesting to note that hydrogen peroxide is capable, under certain conditions, of oxidising sodium butyrate, with the production of a notable yield of succinic acid. The main attack of the oxidising agent is in this case directed to the terminal methyl group, a result somewhat unexpected in view of earlier observations, which showed that oxidation involves the section of the carbon chain nearest to the existing carboxyl group.

One of the few papers dealing with structure which have been noted is a publication[34] on the disputed question of the constitution of meconic acid. The usual view, that the compound is a pyrone derivative, will probably require modification, as, on catalytic reduction under mild conditions, it is converted into tetrahydroxypimelic acid. This result could, of course, be explained on the assumption that, during reduction, the pyrone ring became ruptured, but the behaviour of authentic 4-pyrones, when similarly treated, lends no support to this view. On the whole, even admitting the irregular properties of meconic acid, the suggestion that the compound is a pentahydroxyketopimelic acid,

$$CO_2H\cdot C(OH)_2\cdot CH(OH)\cdot CO\cdot CH_2\cdot C(OH)_2\cdot CO_2H,$$

will be accepted with reserve.

In the course of experiments on the addition of bromine in aqueous solution to unsaturated acids, some interesting results have come to light. The fact, too often ignored, that both bromine and chlorine water contain halogen hydride and the corresponding oxy-acid in equilibrium, naturally complicates such reactions, but it has been shown,[35] in the case of fumaric acid, that the essential result is the formation of bromohydroxysuccinic acid,

$$CO_2H\cdot CH{:}CH\cdot CO_2H \longrightarrow CO_2H\cdot CHBr\cdot CH(OH)\cdot CO_2H,$$

[32] P. A. Levene and C. H. Allen, *J. Biol. Chem.*, 1916, **27**, 433; *A.*, i, 3.
[33] E. Cahen and W. H. Hurtley, *Biochem. J.*, 1917, **11**, 164; *A.*, i, 535.
[34] W. Borsche, *Ber.*, 1916, **49**, 2538; *A.*, i, 117.
[35] E. Biilmann, *Rec. trav. chim.*, 1917, **36**, 313; *A.*, i, 378.

thus emphasising the important part played by hypobromous acid in these additions. Crotonic acid behaves similarly to fumaric acid, and the observation that the normal addition of bromine is favoured by the presence of potassium bromide is consistent with the fact that the equilibrium between halogen hydrides and their oxy-derivatives is displaced by the presence of halogen salts. Other evidence of a different nature pointing to the comparatively large proportion of hypobromous acid present in bromine water has been furnished as a result of estimating the relative amounts of ethylene bromohydrin and ethylene dibromide formed on absorbing ethylene in aqueous bromine.[36]

Halogen acids of the aliphatic series continue to occupy the attention of many investigators, and, as a rule, the object of these inquiries is to gain evidence as to the mechanism of changes in which the substituting halogen atoms are replaced. Considering the frequent anomalies encountered in such reactions, it is not surprising that, as the result of physical studies, many perplexing features are disclosed for which no ready explanation can be found. The observation[37] that, during the action of sodium methoxide on sodium monobromosuccinate, the proportion of bromine ionised exceeds the corresponding decrease in the alkali titre, may no doubt be accounted for on the supposition that intermediate compounds are formed, and this seems to be another feature of β-substituted acids which is not shared by α-isomerides. Naturally enough, considering the interest attached to work of this nature, there is a tendency for researches to overlap to some extent. Thus, the decomposition of bromoacetic acid in alcoholic solution has been studied with results which, with one exception, may be classified as normal.[38] When, however, the change is modified by exposure to powerful light, under conditions which exclude access of alkali, the solvent alcohol and the bromo-acid react so as to give the simple oxidation and reduction products.

$$CH_2Br{\cdot}CO_2H + C_2H_5{\cdot}OH \longrightarrow CH_3{\cdot}CO_2H + CH_3{\cdot}COH + HBr.$$

Another research forming part of a general study of the reactivity of halogen atoms in organic combination[39] deals with the action of alkalis on alkali bromopropionates or bromoacetates, and is less restricted in scope than the paper discussed above in that the effect of solvents in influencing the displacement of the halogen is established.

During the period now under review, comparatively few papers

[36] J. Read and Miss M. M. Williams, *T.*, 1917, **111**, 240; *A.*, i, 313.
[37] E. H. Madsen, *Zeitsch. physikal. Chem.*, 1917, **92**, 98; *A.*, ii, 250.
[38] H. W. Cassel, *ibid.*, 113; *A.*, ii, 249.
[39] G. Senter and H. Wood, *T.*, 1916, **109**, 681; *A.*, 1916, ii, 523.

have been concerned with simple haloids, and, as it is thus impossible to deal with them in a separate section, they may perhaps be discussed at this stage. An old problem, the isomerisation of *iso*butyl bromide, has again been exhaustively studied. When carefully purified, the compound proves to be unexpectedly labile, being transformed with comparative ease into the tertiary isomeride. The change is not only accelerated by various agents, but is retarded by a number of negative catalysts, including *iso*butyl alcohol, so that the real instability of the haloid is not revealed until a high degree of purity is attained.[40] Curiously enough, although *iso*butyl bromide rearranges to the tertiary isomeride in the gaseous state, the change is but little affected by the catalysts which are most reactive in the case of the liquid compound. These observations afford a ready explanation of the results described in a closely related investigation on the dissociation and rearrangement of the isomeric butyl bromides.[41]

Recent studies of organo-metallic compounds are, of course, only distantly connected with the subjects now under discussion, and, in any case, the objective of such work lies within the province of another section of this Report, but it may not be out of place to direct attention to evidence which is strongly in favour of the idea that the four valencies of lead are interequivalent and are probably symmetrically arranged in space.[42]

Esters.

Of the organic reactions which are periodically rediscovered, few can compete with that in which an interchange of alkyl groups takes place between an ester and the solvent alcohol under the influence of metallic alkyloxides. Another instance is forthcoming[43] in the case of ethereal oxalates, which can be interconverted by treatment with the appropriate alcohol containing potassium hydroxide in solution. Reactions of esters, which in the strictest sense are novel, have not been prominent recently, and, in a field so well explored, it is not surprising that much of the current work involving these compounds is of a semi-physical nature and is largely concerned with isomerism or tautomeric changes. Thus, methyl formylphenylacetate has been very

[40] A. Michael, E. Scharf, and K. Voigt, *J. Amer. Chem. Soc.*, 1916, **38**, 653; *A.*, 1916, i, 361.

[41] R. F. Brunel, *ibid.*, 1917, **39**, 1978; *A.*, i, 625.

[42] G. Grüttner and E. Krause, *Ber.*, 1917, **50**, 202; *A.*, i, 256.

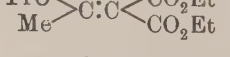
[43] N. C. Qua and D. McLaren, *J. Amer. Chem. Soc.*, 1916, **38**, 1803; *A.*, 1916, i, 709.

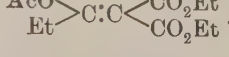
thoroughly examined[44] and its reactions described in great detail. As in the case of the corresponding ethyl compounds, two modifications have been isolated, and the α-form, which is remarkably stable, is regarded as possessing the enolic structure

$$OH\cdot CH{:}CPh\cdot CO_2Me.$$

The β-form is likewise stable and does not seem to be readily transformed into the more reactive α-isomeride, but perhaps the most valuable aspect of the work is the warning issued against a too ready acceptance of evidence as to structure which is based on the colour reaction towards ferric chloride. When dissolved in methyl alcohol, the enolic form of methyl formylphenylacetate gives a positive result with the reagent, but the colour fades, an observation which might be attributed to conversion into the aldo-isomeride. The evidence, however, is, in this case, inconclusive, as a definite methyl alcoholate is formed which gives no coloration with ferric chloride, although, in justice to the colour reaction, it should be stated that this additive compound is doubtless derived from the aldo-form, and its formation is thus a proof of tautomeric change. Our information on the ethereal formylphenylacetates is certainly becoming more definite, but the view that isomeric forms attain a keto-aldo equilibrium in solution is not without its critics.[45]

Clear and well-defined evidence has now been obtained which identifies the labile hydrogen atoms involved when β-diketones or β-ketonic esters undergo enolisation. Selecting the test case of the compound hitherto termed ethyl diacetylmalonate, it has been shown that the irregular constitution ascribed to the substance is no longer tenable. The fact that many properties of the compound, both positive and negative, are not in agreement with the formula $[CH_2{:}C(OH)_2]_2C(CO_2Et)_2$ receives ready explanation from the suggestion that it is in reality the normal acetate of enolic ethyl monoacetylmalonate, $CH_3\cdot C(OAc){:}C(CO_2Et)_2$. The proof on which this claim is based involves the direct preparation of the substance by the acetylation of ethyl acetylmalonate, and also the fact that the acetylation of ethyl propionylmalonate and the propionylation of ethyl acetylmalonate give rise to products, figured below, which are isomeric and not identical.





This disposes of a case, apparently irregular, in which enolisation had involved hydrogen unattached to the carbon atom situated

[44] W. Wislicenus and pupils, *Annalen*, 1916, **413**, 206; *A.*, i, 268.
[45] W. Dieckmann, *Ber.*, 1916, **49**, 2213; *A.*, 1916, i, 820.

between the carbonyl groups, and, in the paper quoted,[46] convincing evidence is produced which refers ethyl acetylmalonate and acetylacetone to enolic structures of normal type.

Still another explanation of the conversion of ethyl acetate into ethyl acetoacetate is rendered possible through the observation that the latter compound is produced from dimeric keten by the action of alcohol containing sodium ethoxide. On this basis, the suggestion is made that the first effect of the sodium used in the reaction is to convert the simple ester into a metallic alcoholate of the keten type, $CH_2{:}C(ONa)\cdot OEt$. In this connexion, it may be remarked that a considerable amount of research is being devoted to ketens generally, and a good case has been made for the claim that dimeric ketens are not, after all, to be regarded as derivatives of *cyclo*butane-1 : 3-dione, although they may be readily transformed into such compounds.[47] In order to settle this point, various *cyclo*butanedione derivatives have been examined and found to respond to the usual ketone reactions, and to differ in practically every respect from the related dimeric ketens. Further studies have also been made of the polymerisation of ketens, and it has been shown that the introduction of the carboxyl group enhances the instability of the compounds. Attempts, based on this special reactivity, to pass directly from a keten-monocarboxylic ester into the corresponding *cyclo*butane derivatives have, so far, met with no success,[48] as substituted pyrones were formed. Work of this description is hampered not only by the experimental difficulties encountered and the instability of the products, but also by the fact that the prediction of even the approximate properties of the compounds is invested with much uncertainty.[49, 50]

The Sugar Group.

The special feature of the past year's publications dealing with the simpler sugars has been the renewed attention paid to optical properties, and more particularly to the phenomenon of mutarotation. On first inspection, there could be no more unpromising field in which to search for relationships between structure and optical rotatory power, but the results accumulated during the past ten years have strengthened the conviction that, in the sugar group, configuration and specific rotation are simply related, and thus optical values may serve as a guide to constitution.

[46] K. von Auwers and E. Auffenberg, *Ber.*, 1917, **50**, 929 ; *A.*, i, 627.
[47] G. Schroeter and pupils, *ibid.*, 1916, **49**, 2697 ; *A.*, i, 145.
[48] H. Staudinger and H. Becker, *ibid.*, 1917, **50**, 1016 ; *A.*, i, 629.
[49] H. Staudinger and H. Hirzel, *ibid.*, 1024 ; *A.*, i, 630.
[50] H. Staudinger and H. Hirzel, *ibid.*, 1916, **49**, 2522 ; *A.*, i, 178.

At the same time, mutarotation continues to display ever-increasing complications, but its study, as is inevitably the case where exact physical measurements are concerned, has resulted in the development of improved methods for preparing and purifying the compounds examined. These considerations have been apparent in directing much of the current work on sugars. Thus, it has been shown [51] that glucose of exceptional purity may be obtained by using acetic acid as a crystallising medium, and that, moreover, either the α- or β-form may be separated by modifying the conditions of solution. In the writer's experience, the use of acetic acid is most effective, and, in the case of β-glucose, is somewhat more convenient than the older method of crystallising from pyridine. The latter method, however, still continues to be used successfully.[52, 53]

Another sugar preparation to which attention should be directed is that of mannose, which can be obtained by acid hydrolysis of vegetable ivory, and may even be isolated in the solid form without the intermediate formation of the phenylhydrazone.[54] This marks a very substantial step, as research on mannose has always been restricted by the comparative inaccessibility of the pure crystalline sugar. The above examples, although typical, do not by any means exhaust the list of improved methods of preparation which have recently been described, but they are sufficiently striking to indicate one of the indirect benefits conferred by the study of mutarotation.

Turning to some of the optical results which have been described, special interest will be taken in new data contributed in support of Hudson's generalisation affecting the molecular rotations of α and β-forms of sugars. The essential feature of Hudson's view, namely, that the difference between the molecular rotations of the α- and β-forms of mutarotatory sugars is a constant, is now widely accepted, and has recently been put to the test in the case of thirteen natural or synthetic sugars.[55] The compounds selected show considerable diversity of type, yet, on the whole, the generalisation is well supported. Somewhat discordant results were obtained with mannose, lyxose, and rhamnose, although, in the case of the last-mentioned sugar, this is not surprising. It may

[51] C. S. Hudson and J. K. Dale, *J. Amer. Chem. Soc.*, 1917, **39**, 320; *A.*, i, 320.

[52] A. W. Mangam and S. F. Acree, *ibid.*, 965; *A.*, i, 446.

[53] J. E. Mackenzie and S. Ghosh, *Proc. Roy. Soc. Edin.*, 1916, **36**, iii, 204; *A.*, i, 79.

[54] C. S. Hudson and H. L. Sawyer, *J. Amer. Chem. Soc.*, 1917, **39**, 470; *A.*, i, 321.

[55] C. S. Hudson and E. Yanovsky, *ibid.*, 1013; *A.*, i, 445.

be remarked that the initial values of the specific rotations quoted in the paper were arrived at by the indirect method based on solubility measurements,[56, 57] and new maximum values have in this way been attached to several common sugars.

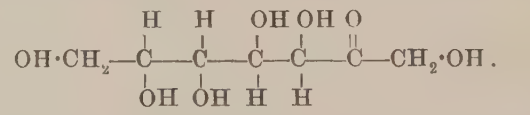
An important extension of Hudson's views is marked by the appearance of a paper[58] in which the specific rotations of the phenylhydrazides derived from acids related to the sugars are compared. Analysis of the data shows that the asymmetric system attached to the α-carbon atom exerts a preponderating influence on the activity of these compounds and determines the sign of the rotation. The result has been substantiated from other sources,[59, 60] and another example has thus been added to the cases in which the polarimeter serves as a guide to structure. The search for simple optical generalisations of this nature is a development which is certain to attract many workers, and signs are not wanting that the quest is being extended.[61]

With regard to the action of reagents on simple sugars, there is little to report. Attempts to isolate definite thio-derivatives of glucose have been continued, but have met with scant success.[62] On the other hand, in a closely related topic, an interesting result has been obtained in decomposing glucose ethylmercaptal by one molecular proportion of mercuric chloride.[63] The reaction yielded a crystalline ethylthioglucoside, which presumably has the structure

$$OH\cdot CH_2\cdot CH(OH)\cdot CH\cdot[CH\cdot OH]_2\cdot CH\cdot SEt$$
$$\qquad\qquad\qquad

impression that sugars are readily characterised by means of their osazones, and it is not surprising to find that research is still applied to the discovery of well-defined sugar derivatives suitable for identification. *p*-Tolylhydrazine has been used to some extent,[65, 66] but many of the products show an undesirable tendency to melt at practically the same temperature. This objection does not apply so forcibly to the use of diphenylmethanedimethyldihydrazine, which appears to act in precisely the cases in which phenylhydrazine gives inconclusive results.[67, 68]

The discovery of two new natural sugars is in itself noteworthy, but particularly so when both compounds belong to the heptose series. From the aqueous extract of the avocado pear, a crystalline mannoketoheptose has been isolated which shows the normal properties of a reducing sugar, although it has not yet been separated into mutarotatory forms.[69] Complete evidence as to structure was obtained by reduction and osazone formation, and points to the configuration



The sugar is not fermentable by yeast, and the same holds true for sedoheptose, which has been isolated from the leaves and stems of *Sedum spectabile*.[70] Not the least interesting feature of the latter heptose is the apparent ease with which it is converted into an anhydro-derivative by processes which are much less drastic than those necessary for the formation of anhydroglucose.

Although during the past year research on standard lines has obviously been somewhat limited so far as reducing sugars are concerned, much attention has been paid to problems which have a more immediate bearing on existing conditions. Of these, only one need be mentioned here. Commercial syrupy glucose has long been recognised as a highly complex mixture, but it will come as a surprise to many to learn that the glucose content of average samples may be as low as 12 per cent., and that the proportion of maltose present generally exceeds that of glucose.[71]

[65] A. W. van der Haar, *Rec. trav. chim.*, 1917, **36**, 346; *A.*, i, 380.
[66] *Ibid.*, 1917, **37**, 108; *A.*, ii, 515.
[67] E. Votoček, *Ber.*, 1917, **50**, 35; *A.*, i, 250.
[68] J. von Braun, *ibid.*, 42; *A.*, i, 251.
[69] F. B. La Forge, *J. Biol. Chem.*, 1917, **28**, 511; *A.*, i, 118.
[70] F. B. La Forge and C. S. Hudson, *ibid.*, **30**, 61; *A.*, i, 444.
[71] J. A. Wesener and G. L. Teller, *J. Ind. Eng. Chem.*, 1916, **8**, 1009; *A.*, i, 7.

Glucosides.

The synthesis of glucosides by the agency of tetracetylbromoglucose still gives profitable results, and the work is marked by one or two features which are worthy of note.

Mention should be made, in the first instance, of the success attending Fischer's efforts to synthesise mandelonitrile-glucoside, which has been obtained in the racemic form and also in the *d*- and *l*-varieties. The key to the synthesis is the use of ethyl *dl*-mandelate in the reaction with tetracetylbromoglucose, a proceeding which limits the condensation to the hydroxyl group. Thereafter, the racemic product is converted into the mixture of amides, which are separable by crystallisation into the two active forms. After dehydration, so as to produce the corresponding nitriles, the acetyl groups are removed by the action of ammonia, and, although the change is accompanied by racemisation, this enabled the resulting *dl*-mandelonitrile-glucoside to be identified with natural prulaurasin.

The ultimate resolution does not seem to have been unduly troublesome, and both *d*- and *l*-mandelonitrile-glucosides were ultimately obtained. The former proved to be identical with sambunigrin, and this result by no means exhausts the features of a highly important paper.[72]

As is well known, when tetracetylbromoglucose enters into reaction with an alcohol or phenol, the liberated hydrobromic acid generally effects the gradual removal of the substituting acetyl groups, and thus complex mixtures are formed which are troublesome to separate. To overcome this difficulty, quinoline, or even soluble alkaloids, may be employed, and the efficiency of the former reagent is well marked in some of the recent work described by Fischer. For example, the glucosides of phenol,[73] menthol, and resorcinol[74] have been obtained by this method, and it would appear that the work is being carried out with the ultimate object of preparing glucosides of physiological importance. This is a most desirable development, as only too frequently the synthesis of glucosides appears to be directed merely to the preparation of new compounds of little permanent value. At the same time, the idea that glucosides are uniformly more reactive physiologically than the parent substances has not been well maintained, and to the numerous exceptions already recognised may be added the case

[72] E. Fischer and M. Bergmann, *Ber.*, 1917, **50**, 1047; *A*., i, 657.
[73] E. Fischer and L. von Mechel, *ibid.*, 1916, **49**, 2813; *A.*, i, 216.
[74] E. Fischer and M. Bergmann, *ibid.*, 1917, **50**, 711; *A.*, i, 467.

of the glucoside of dihydrocupreine.[75] Although they are interesting compounds, the alkaloidal glucosides as a class have been but little studied, and this is not surprising, as, judging from results, their examination by ordinary methods can give but little satisfaction.[76]

A slight variation of the customary type of glucoside synthesis is introduced by the interaction of tetracetylbromoglucose with the silver salts of organic acids. The acetylated glucose esters thus produced are peculiarly prone to undergo hydrolysis, and attempts to remove the acyl groups resulted in complete rupture of the complexes. The work has nevertheless yielded one interesting observation, in that, when silver salicylate is used in the condensation, two isomeric substances are formed.[77] Of these, one is the expected salicylate of tetra-acetylglucose, whilst the other is a salicylic acid tetra-acetylglucoside. From this result, the reasonable conclusion is drawn that silver salicylate exists in two modifications,

$$C_6H_4\langle^{CO_2Ag}_{OH} \qquad \text{and} \qquad C_6H_4\langle^{CO_2H}_{OAg},$$

and, in view of the behaviour generally of the silver salts of hydroxy-acids, it would actually appear that in such compounds the metallic atom is distinctly labile and can react either in the carboxy- or hydroxy-position.

Disaccharides and Polysaccharides.

Authentic syntheses of disaccharides by biochemical agency is making gradual progress, and the results will be more widely appreciated now that definite crystalline compounds are being isolated from syrupy mixtures. The characterisation of two mutarotatory galactobioses[78,79] marks a distinct step and gives promise that, in this way, more light will be shed on the complex problem of how monosaccharides are structurally linked. Already there seems good grounds for the belief that our blackboard illustrations will soon require modification in this respect. Other research on disaccharides has, on the whole, followed normal lines and discloses few outstanding features.

One exception to this statement is presented by the synthesis

[75] P. Karrer, *Ber.*, 1916, **49**, 1644; *A.*, 1916, i, 832.
[76] A. Heiduschka and H. Sieger, *Arch. Pharm.*, 1917, **255**, 18; *A.*, i, 407.
[77] P. Karrer, *Ber.*, 1917, **50**, 833; *A.*, i, 539.
[78] E. Bourquelot and A. Aubry, *Compt. rend.*, 1917, **164**, 521; *A.*, i, 250.
[79] *Ibid.*, 443, *A.*, i, 250.

of the sulphur and selenium analogues of *iso*trehalose.[80] Starting from that invaluable reagent tetra-acetylbromoglucose, the action of potassium hydrogen sulphide in alcoholic solution couples the two hexose residues through the sulphur atom, and, by the agency of alcoholic ammonia, the acyl groups were then eliminated. The thio*iso*trehalose thus formed is a definite crystalline compound which is notably stable towards mineral and organic hydrolysts, and the same holds true for the corresponding selenium derivative. Even admitting that the formation of these disaccharide analogues appears to have been accidental, their discovery is not without importance.

From year to year great variation is shown in the number of papers dealing with polysaccharides, and the period under review has been more fruitful than usual, although, naturally enough, the results described are often vague and obscure. Among the more definite investigations may be noted a further study of the trimethylglucose obtained from methylated cellulose by hydrolysis.[81] The compound in question may be regarded as a fragment of the cellulose complex in which the original hydroxyl groups are alkylated, and thus the structure becomes an important consideration. For various reasons, the constitution is represented by

$$OMe\cdot CH_2\cdot CH(OH)\cdot CH\cdot CH(OMe)\cdot CH(OMe)\cdot CH\cdot OH$$
$$\qquad\qquad\qquad

Optical Activity.

As stated in the preceding section of this Report, much recent work on optical activity has been concerned with members of the sugar group, and as many of the results have a structural application, they are appropriately described under carbohydrates. With reference to optical activity generally, somewhat new ground is being opened up by the collection of data as to the specific rotations of optically active ketones and diketones, but the work has not proceeded far enough to render possible more than qualitative relationships between structure and rotatory power.[86] In other fields, however, a number of definite observations have been made, and in the first instance attention may be directed to the successful preparation of diaminoglycerol in *d*- and *l*-forms.[87] Inspection of the Reports for the past two years will give an idea of the research of which this forms part, and of the special difficulties encountered in previous attempts to obtain the desired active compound.

Starting from optically active glycerol $\alpha\beta$-dibromohydrin, reactions designed to displace the halogen atoms by amino-groups resulted uniformly in the destruction of the asymmetric system.*

This difficulty has now been got over by deferring resolution until after the introduction of the amino-groups into the required positions, so that the synthetical scheme commences with methyl allyl ether. The various stages are summarised below:

$$CH_2{:}CH{\cdot}CH_2{\cdot}OMe \xrightarrow[Br_2]{} CH_2Br{\cdot}CHBr{\cdot}CH_2{\cdot}OMe \xrightarrow[\text{alcoholic } NH_3]{}$$
$$\text{inactive } CH_2(NH_2){\cdot}CH(NH_2){\cdot}CH_2{\cdot}OMe \longrightarrow$$
$$d\text{- or } l\text{-}CH_2(NH_2){\cdot}CH(NH_2){\cdot}CH_2{\cdot}OMe \xrightarrow[HBr]{}$$
$$d\text{- or } l\text{-}CH_2(NH_2){\cdot}CH(NH_2){\cdot}CH_2{\cdot}OH.$$

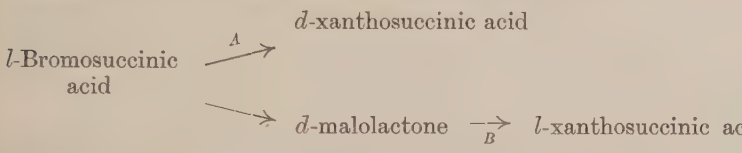
The reaction between the dibromohydrin and ammonia gave very poor yields, and the resolution, which was carried out on the diaminomethoxypropane, appears to have given trouble, but the result is a triumph over a combination of severe experimental difficulties. The appreciation of the writer is in no way diminished by the fact that, some years ago, in an attempt to solve the constitution of glycerol methyl ether, he attempted precisely the same series of reactions, but without success.

[86] H. Rupe and S. Wild, *Annalen*, 1917, **414**, 111; *A.*, i, 538.

[87] E. Abderhalden and E. Eichwald, *Ber.*, 1916, **49**, 2095; *A.*, 1916, i, 795.

* In the Report for 1916 (p. 74) the inactive diaminohydroxypropane obtained by Abderhalden was incorrectly described as being internally compensated, a mistake for which the writer of the Report is alone responsible. —J. C. I.

The application of physical methods to the study of optical activity is on the increase, and is contributing to the formation of clearer views as to the mechanism of optical inversions. Under this heading, reference should be made to some results obtained in converting active bromosuccinic acid into the corresponding thiolmalic acids and xanthosuccinic acids. In the case of the latter compounds, the reaction has been shown[88] to proceed in two different ways, one direct and the other through the intermediate agency of the active lactone of malic acid.



Reaction *A* is thus one of direct substitution, whilst *B* involves addition of potassium xanthate to the lactone. The two reactions, although simultaneous, proceed at different speeds, and the change can be controlled so that successive crops of the product show a diminishing dextrorotation until ultimately the sign of activity is reversed. Obviously in one of these competing reactions a stereochemical change must take place, and, as the result of a carefully conceived series of tests, the conclusion is drawn that the change in question occurs during the direct replacement of bromine.

$$l\text{-}CO_2H\cdot CHBr\cdot CH_2\cdot CO_2H + KS\cdot CS\cdot OEt \longrightarrow d\text{-}CO_2H\cdot CH(S\cdot CS\cdot OEt)\cdot CH_2\cdot CO_2H.$$

Most of the results summarised above are based on the determination of reaction velocities, but other physical measurements can also be used to good effect in studying optical transformations. Thus, as an extension of previous work on similar lines, the systematic determination of the dissociation constants of phenylbromoacetic and phenylbromopropionic acids has been undertaken[89, 90] as part of a general study of the Walden inversion. In this connexion, attention should be directed to fresh results on the effect of solvent media in influencing these optical changes. Taking as a test case the conversion of phenylchloroacetic acid into the corresponding amino-compound, the reaction has been conducted in twelve different solvents, with results which show that inversion occurs in half of the examples studied. The behaviour of water and liquid ammonia as solvents is shown generally to be similar, although, in the latter case, the pre-

[88] B. Holmberg, *Arkiv. Kem. Min. Geol.*, 1916, **6**, No. 8; *A.*, i, 115.
[89] G. Senter and S. H. Tucker, *T.*, 1916, **109**, 690; *A.*, 1916, ii, 524.
[90] G. Senter and G. H. Martin, *ibid.*, 1917, **111**, 447; *A.*, ii, 301.

dominant reaction is accompanied by the formation of iminodiphenyldiacetic acid.[91]

Many synthetical possibilities are involved in the use of optically active glyceraldehyde, and some recent results are worthy of note. It appears[92] that *d*-glyceraldehyde dimethylacetal is somewhat more stable than might have been expected from the nature of these compounds, and, for complete hydrolysis, requires the use of 0·1 *N*-sulphuric acid at 50°. The active product thus obtained, when subjected to the cyanohydrin reaction and subsequent hydrolysis, gives a mixture of active acids. On oxidation of the primary alcohol group, *l*-tartaric acid is the only active product isolated, so that it is now possible to correlate the active glyceraldehydes with *d*-glucose and to apply to the former compounds the expressions *d*- and *l*-, according to the conventional system. As the dextrorotatory form of the aldehyde is the variety which gives *l*-tartaric acid, it is regarded as the *d*-compound related to *d*-glucose.

Even to those who have no personal experience in work on optical activity, it must be evident that few branches of research present greater difficulties. Inversion effects, racemisation, and the uncertainty of deciding when a compound is optically pure or optically homogeneous, are obstacles which frequently have to be faced, but when special experimental difficulty is encountered in the preparation of test compounds, the prospects are not encouraging. The latest contribution to the optical study of the diphenylsuccinic acids furnishes a case in point, as work designed to convert the *meso*-ester into a mixture of the active acids in unequal amounts broke down through the unexpected stability of the *l*-menthyl esters. Not only so, but the formation of the normal menthyl esters of the active acids was accomplished only in one case, and even such a trustworthy reagent as thionyl chloride failed to overcome this difficulty.[93]

Nitrogen Compounds.

During the period now under review, publications dealing with nitrogen compounds have been numerous, and it has been a matter of more than usual difficulty to draw even an approximate line where true aliphatic compounds end and heterocyclic compounds begin. The policy, recently followed, has therefore been con-

[91] G. Senter and H. D. K. Drew, *T.*, 1916, **109**, 1091; *A.*, 1916, i, 815.
[92] A. Wohl and F. Momber, *Ber.*, 1917, **50**, 455; *A.*, i, 319.
[93] H. Wren and C. J. Still, *T.*, 1917, **111**, 513; *A.*, i, 456.

tinued of limiting consideration, as far as possible, to compounds which are essentially open-chain structures.

The preparation and study of simple amines has occupied a prominent place in recent literature, and reference has already been made to an explanation which has been put forward to account for the formation of mono- and di-methylamines by the agency of formaldehyde. In addition, the method of preparing amines which is based on the interaction of potassium phthalimide and chloro-compounds has been considerably modified as the result of the observation that, when applied to α-chloro-*n*-propyl alcohol, the product formed is a derivative, not of *iso*propylamine, but of *n*-propylamine. Investigation of this abnormal reaction has shown[94] that the first stage is the removal of hydrogen chloride, with the consequent formation of propylene oxide, which then combines additively with a molecule of phthalimide.

$$CH_3\cdot CHCl\cdot CH_2\cdot OH \longrightarrow CH_3\cdot \underset{\diagdown O \diagup}{CH}\text{–}CH_2 \longrightarrow$$

$$CH_3\cdot CH(OH)\cdot CH_2\cdot N\langle \begin{matrix} CO \\ CO \end{matrix} \rangle C_6H_4 \longrightarrow CH_3\cdot CH(OH)\cdot CH_2\cdot NH_2.$$

This has resulted in the use, in the same general reaction, of preformed alkylene oxides, several of which have been found to react with potassium phthalimide[95] to give ultimately primary amines. By the use of such compounds as epichlorhydrin in place of an unsubstituted oxide, a phthalimide derivative of the type

$$CH_2Cl\cdot CH(OH)\cdot CH_2\cdot N\langle \begin{matrix} CO \\ CO \end{matrix} \rangle C_6H_4.$$

is obtained, and as chlorine can be readily displaced by bromine in this compound, it will at once be seen that the synthetical possibilities thus opened out are very numerous. Other routes to brominated amines are, of course, possible, and, in example, the cases may be cited in which bromoethylamine[96] and bromo*iso*propylamine[97] have been prepared from the corresponding amino-alcohols. Before leaving the subject of amines, it may perhaps be noted that fresh complications have been added to the problem as to the function of small quantities of iron and free acid in reducing nitro-compounds. It has been stated[98] that nitro-paraffins are reduced to the corresponding amines by this agency,

[94] S. Gabriel and H. Ohle, *Ber.*, 1917, **50**, 804; *A.*, i, 563.
[95] S. Gabriel and H. Ohle, *ibid.*, 819; *A.*, i, 565.
[96] S. Gabriel, *ibid.*, 826; *A.*, i, 541.
[97] S. Gabriel, *ibid.*, 1916, **49**, 2120; *A.*, 1916, i, 794.
[98] H. Krause, *Chem. Zeit.*, 1916, **40**, 810; *A.*, 1916, i, 793.

even when the system is allowed to become alkaline, and in such cases it is evident that ferrous hydroxide rather than ferrous chloride must be regarded as one of the effective reducing agents. So far as efficiency is concerned, the process mentioned above is in no sense inferior to catalytic methods for reducing nitro-compounds. In this connexion, mention may be made of the indirect production of primary amines from alkyl nitrites, by reduction under conditions which lead to the transient formation of the corresponding nitro-compounds.[99]

Considering the importance of reactions involving silver salts and alkyl haloids, and the so-called "abnormalities" displayed by silver cyanide in particular, new ideas on the structure of the latter compound are welcome. From the fact that silver cyanide and methyl iodide react at the ordinary temperature to give $(AgNC)_2,MeI$, whilst at 40° the product contains an additional molecule of the haloid, and is doubtless $(AgNC,CH_3I)_2$, the suggestion has been made[1] that the silver salt may be represented by the structure $Ag{\cdot}N{:}C{:}N{\leqslant}^{C}_{Ag}$. This idea certainly accounts for the successive addition of two molecules of methyl iodide, and appears to be consistent with many other reactions of the salt.

Considerable interest will be taken in the marked revival of work on aliphatic diazo-compounds, no fewer than eleven consecutive papers on this subject being contributed by Staudinger and his pupils. In dealing with a mass of experimental results, which is almost unwieldy, the desirable policy has been followed by the author of prefacing the series of publications by a general introduction.[2]

The methods of preparation adopted involved either the use of nitrosomethanes on modified lines or the mild oxidation of appropriate hydrazones, and the properties of a considerable number of new diazo-compounds have now been described. Most of these are substituted diazomethanes, and special attention has been paid to diphenyldiazomethane, which appears to be comparatively stable.[3]

Although it readily gives the normal reactions of such compounds, attempts to utilise the reagent for the production of diphenylsulphen met with no success. Nevertheless, in order to account for the products actually formed, a suggestive structural

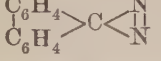
[99] P. Neogi and T. C. Chowdhuri, *T.*, 1917, **111**, 899; *A.*, i, 686.

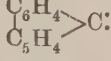
[1] E. G. J. Hartley, *ibid.*, 1916, **109**, 1296; *A.*, i, 83.

[2] H. Staudinger, *Ber.*, 1916, **49**, 1884; *A.*, 1916, i, 847.

[3] H. Staudinger, E. Anthes, and F. Pfenninger, *ibid.*, 1928; *A.*, 1916, i, 851.

scheme has been forthcoming which involves the transient formation of the desired $CPh_2{:}SO_2$.[4] Research on a number of constitutional problems has also been undertaken in the course of the work, and amongst these may be mentioned a study of the action of hydrogen sulphide on diazo-compounds generally. The fact that under the influence of this reagent most diazo-compounds are reduced to hydrazones has in the past been used as an argument for assigning derivatives such as diazo-anhydrides to a different structural type. It is now shown, however,[5] that, in addition to hydrazone formation, other reactions resulting in the production of thiols or thiodiazole derivatives may occur, and, such being the case, there seems no good reason for discriminating sharply between true diazo-compounds and diazo-anhydrides. Another ingenious structural scheme has been used as the basis of attempts to synthesise a second form of diphenylenediazomethane, and thus secure a representative for each of the rival formulæ:





This, unfortunately, broke down,[6] but the results may be interpreted as furnishing additional arguments for the open-chain structure.

The action of acid chlorides on diazo-esters has also been studied,[7] and the reaction given by ethyl diazoacetate appears to be typical in that two ester molecules react unequally, as shown below:

$$\begin{matrix}CHN_2\cdot CO_2Et\\ CHN_2\cdot CO_2Et\end{matrix} + R\cdot COCl \longrightarrow CH_2Cl\cdot CO_2Et + N_2 + R\cdot CO\cdot CN_2\cdot CO_2Et.$$

It is evident that, in the aliphatic diazo-series, generalisations are hard to find. Great variety is shown even in the colour of the compounds, but there seems to be no definite relationship between colour and stability, so that even in this respect speculations on structure have been necessarily restricted. Our views of the constitution of these compounds are thus still uncertain, and if Staudinger is content to compromise between the cyclic and open-chain types, few will be inclined to dispute his opinion.

Another lengthy series of papers, dealing particularly with the azides and hydrazides of aliphatic hydroxy-acids, has appeared from Curtius' laboratory. The usual methods of preparation have been adopted and the results are normal, but, in the case of lower

[4] H. Staudinger and F. Pfenninger, *Ber.*, 1916, **49**, 1941; *A.*, 1916, i, 852.
[5] H. Staudinger and J. Siegwart, *ibid.*, 1918; *A.*, 1916, i, 849.
[6] H. Staudinger and A. Gaule, *ibid.*, 1961; *A.*, 1916, i, 853.
[7] H. Staudinger, J. Becker, and H. Hirzel, *ibid.*, 1978; *A.*, 1916, i, 855.

members, the actual products are ill-defined, although their derivatives crystallise well.[8] This naturally places restrictions on detailed discussion.

Carbamides.—From a publication which appeared during the year,[9] it would seem that the reaction between nitrous acid and carbamide has been too readily accepted as following the usual course in which primary amino-groups are eliminated by this reagent. In the particular case of carbamide, nitrogen and carbon dioxide should be evolved in the volumetric proportion of two to one, but in practice this is never realised, thus pointing either to an entirely different mechanism of reaction or to the occurrence, in notable degree, of scondary changes in which part of the nitrogen is retained. The decomposition with nitrous acid, moreover, only takes place in the presence of an acid which combines with urea, so that, strictly speaking, the reaction is confined to salts. In addition, cyanic acid has now been detected as one of the primary products of the change, and this intermediate compound may undergo subsequent decomposition, the nature of which varies according to the conditions. Under the action of excess of nitrous acid, carbon dioxide and nitrogen are eliminated, but with low concentrations, ammonia is formed by simple hydrolysis. The combined results are held to be consistent with the ring structure for urea, but the whole problem of the reaction between nitrous acid and cyclic compounds conforming to the betaine type is beset with difficulties.

The equally complex problems presented by thiocarbamide have also been the subject of considerable research, and the number of additive salts isolated has been enlarged,[10] whilst the reaction between thiocarbamide hydrochloride, and acetaldehyde has been ascribed to a curious change in which the salt-forming acid molecule migrates from the base to the aldehyde.[11] These observations on salt-formation are of importance as a further step towards localising the intramolecular changes in thiocarbamide, and have been considerably extended in another paper,[12] to which appreciative reference should be made. Additive compounds of thiocarbamide and alkyl haloids have been known and studied for a considerable time, and it has now been shown that the alkyl salts of inorganic acids are similarly capable of direct union with the base. On the other hand, esters of organic acids do not combine

[8] T. Curtius, *J. pr. Chem.*, 1917, [ii], **95**, 168; *A.*, i, 635.
[9] E. A. Werner, *T.*, 1917, **111**, 863; *A.*, i, 639.
[10] A. E. Dixon, *ibid.*, 684; *A.*, i, 545.
[11] A. E. Dixon and J. Taylor, *ibid.*, 1916, **109**, 1244; *A*, i, 11.
[12] J. Taylor, *ibid.*, 1917, **111**, 650; *A.*, i, 514.

directly with thiocarbamide, but this difficulty has been overcome by double decompositions in which thiocarbamide methyl sulphate has been successfully employed. The structure of these additive compounds admits of at least three possibilities, but strong evidence exists which favours the constitution

$$\begin{matrix} NH_2 \\ NH_2 \end{matrix}\!\!>\!C\!:\!S\!<\!\!\begin{matrix} R \\ X \end{matrix},$$

where R denotes an alkyl group. Another interesting feature of the same paper is the isolation of thiocarbamide benzyl sulphate in a new form, which is interconvertible with the variety previously known. This result does not stand alone by any means, but the isomeric varieties of these and similar derivatives may be satisfactorily accounted for by reference to "sulphonium" or "ammonium" types.

Further evidence bearing on the constitution of thiocarbamide and related compounds is furnished by the somewhat unexpected reactions which they display towards mercuric nitrite.[13] The changes undergone are complex, and in the particular case of thiocarbamide involve the successive reaction of two molecules of the metallic nitrite, followed by the disengagement of nitrous anhydride. Incidentally, it may be remarked that one outcome of the work now referred to is the isolation of definite compounds containing several sulphur atoms in direct attachment, and in which interesting examples of the variations in the sulphur valencies can be traced.

Turning to a related subject, it has been found that when thiocarbamide is dissolved in aqueous alcoholic ammonia, and is thereafter treated with mercuric oxide, guanidine is formed in small quantities in addition to polymerised cyanamide. The latter compound originates in monomeric cyanamide, some of which evidently escapes polymerisation through reaction with ammonia.[14] These changes are best explained by the adoption of the formula $N{:}C{\cdot}NH_2$ for cyanamide, and this view is strongly supported by the molecular refraction values determined for cyanamide and its alkyl derivatives.[15]

Amino-acids.—In last year's Report, brief reference was made to work which had been commnced on the action of chloroamines on proteins and amino-acids, and a further publication on similar lines is forthcoming.[16] It is now evident that "chloramine-T" has to be regarded as a chemical reagent of considerable utility, and

[13] P. C. Rây, *T.*, 1917, **111**, 101; *A.*, i, 194.
[14] E. Schmidt, *Arch. Pharm.*, 1916, **254**, 626; *A.*, i, 449.
[15] E. Colson, *T.*, 1917, **111**, 554; *A.*, i, 448.
[16] H. D. Dakin, *Biochem. J.*, 1917, **11**, 79; *A.*, i, 542

may well play a useful part in the formation of compounds which are somewhat inaccessible. Thus, sodium glutamate may be converted into either β-aldehydopropionic acid or β-cyanopropionic acid, according to the proportions of the reagent used, and numerous other examples are quoted which indicate that by this agency semi-aldehydes may be rendered more available.

Before leaving the subject of the decomposition of amino-acids, mention may be made of a related topic which, although belonging to another section of this Report, should not pass unnoticed. The point will not be disputed that future developments in the chemistry of proteins will depend largely on improvements in conducting the fermentative degradation of polypeptides, as it is only by selective graded hydrolysis that the overwhelming isomerism of such compounds is likely to be elucidated. Although these complexities are generally recognised, the point is emphasised by recent calculations of the number of possible isomeric forms of simple polypeptides.[17] Special interest is thus attached to the systematic attempt now being made to secure accurate conditions, controlled by physical methods, under which enzyme action on polypeptides should be conducted.[18]

It is satisfactory that the revival of synthetical work in this field still continues. Two years ago, reference was made to the improved method of obtaining the *N*-methyl derivatives of *d*-alanine and related acids under conditions which exert no disturbing influence on configuration. This opens out the possibility of a partial resumption of synthetical work without the indecision as to structure attending all reactions which may be accompanied by Walden inversions. Thus, *l*-α-bromopropionic acid reacts with methylamine[19] in the same steric sense as with ammonia, as it gives *l*-*N*-methylalanine. Several other examples are quoted which give promise that, in the synthesis of amino-acid complexes, some control may be maintained of the configuration changes involved.

As is well known, during the hydrolysis of natural proteins, varying amounts of carbon dioxide and ammonia are formed, and although there are many potential sources of these products, analogous cases are furnished by synthetic polypeptides of a modified nature. As an issue of investigations on acid azides, complexes have been isolated which contain diamides coupled with amino-acid residues, and these compounds on hydrolysis give ammonia, amines, and carbon dioxide, in addition to the parent

[17] E. Fischer, *Zeitsch. physiol. Chem.*, 1917, **99**, 54; *A.*, i, 381.

[18] E. Abderhalden and A. Fodor, *Fermentforschung*, 1916, **1**, 533; *A.*, i, 306.

[19] E. Fischer, and L. von Mechel, *Ber.*, 1916, **49**, 1355; *A.*, 1916, i, 802.

amino-acids. This observation has led to the synthesis of new examples of such complexes, the experimental method followed being a combination of two known processes. Starting from an acid azide, this is converted into the corresponding carbimide, which, in turn, is coupled with the ester of an amino-acid. Thereafter, by consecutive formation of the hydrazide and azide, a new carbimide is obtained, which is capable of further reaction with a second amino-acid molecule. The steps of the synthesis are illustrated below in the case of a typical example:

$$\text{Hippuric acid} \longrightarrow CH_2(NHBz)\cdot CO\cdot NH\cdot NH_2 \longrightarrow CH_2(NHBz)\cdot CO\cdot N_3 \longrightarrow CH_2(NHBz)\cdot N{:}CO \xrightarrow[\text{ethyl glycine}]{} CH_2(NHBz)\cdot NH\cdot CO\cdot NH\cdot CH_2\cdot CO_2Et.$$

The free ester group in the last compound formulated above is then converted into the corresponding acethydrazide, on which the series of reactions can be recommenced.[20] The scheme is certainly ingenious as a variation of ordinary polypeptide synthesis, and the products behave on hydrolysis in the expected manner, in that carbon dioxide and ammonia are produced in addition to the normal products. Another example of the preparation of a "mixed" polypeptide is furnished by the successful synthesis of tyrosylglycine–hydantoin,[21] and, in this case also, hydrolysis gives a series of products closely resembling those obtained from proteins.

Much sympathy will follow the examination of known polypeptides and the preparation of new representatives, which has as its object the identification of the precise position in the molecule occupied by any particular amino-acid residue. The constructive units of the scheme are thus amino-acids, which possess diagnostic reactions suitable for identification purposes, but, in addition, attempts are being made to determine the position of free amino-groups in the complexes.[22] This is accomplished by introducing the naphthalenesulphonyl group into the amino-position, and as the substituting group is not readily removed by hydrolysis, it persists in the cleavage products. To take a case in point, if diglycylcystine is converted into the corresponding di-β-naphthalenesulphonyl derivative, treatment of the latter with hydrochloric acid gives cystine and β-naphthalenesulphonylglycine. This at once indicates that the glycyl residues in diglycylcystine preserve the amino-groups intact. The process bears a certain resemblance

[20] T. Curtius, *J. pr. Chem.*, 1916, [ii], **94**, 85; *A.*, i, 199.

[21] T. B. Johnson and Miss D. A. Hahn, *J. Amer. Chem. Soc.*, 1917, **39**, 1255; *A.*, i, 475.

[22] E. Abderhalden and E. Wybert, *Ber.*, 1916, **49**, 2449, 2838; *A.*, i, 119.

to the method of establishing the structure of sugar derivatives by methylation, followed by hydrolysis.

After tedious synthesis, it is often the fate of an organic compound to be promptly destroyed, and this seems to have been the case with a number of synthetic betaines[23] of the type

$$\begin{matrix} R\cdot CH\text{---}CO \\ | \quad\quad | \\ N(Me)_3\cdot O \end{matrix}$$

When decomposed by heating, these compounds invariably yield α-unsaturated acids, and this is a result not without significance, as acids of the same class are common plant products which are generally associated in the living organism with tertiary amines. In all probability, the future study of betaines will do much to throw light on the fate of nitrogenous compounds in plants and the mechanism of their transformations.

In closing this section of the Report, it should be stated that access to most of the original papers has been restricted, and it has been necessary in many cases to work almost entirely from the abstracts. Whenever possible, these have been compared with the originals, and the writer feels that, on this occasion, as in each of the preceding four years, he owes much to the abstractors. It may not be out of place to express this indebtedness.

JAMES COLQUHOUN IRVINE.

PART II.—HOMOCYCLIC DIVISION.

Reactions.

Halogenation.—Bromination and iodination of aromatic hydrocarbons can be effected readily by the action of bromine and iodine in the presence of nitric acid,[1] whilst iodination of phenols and nitrophenols can be carried out in quantitative yield by means of nitrogen iodide or by a solution of iodine in potassium iodide in conjunction with ammonia.[2]

Reduction.—The wider use of ferrous sulphate and ammonia for reducing nitro-compounds has been advocated,[3] and reduction in

[23] S. Komatsu, *Mem. Coll. Sci. Kyōtō*, 1916, **1**, 369; *A.*, i, 139.

[1] R. L. Datta and N. R. Chatterjee, *J. Amer. Chem. Soc.*, 1916, **38**, 2545; 1917, **39**, 435; *A.*, i, 15, 327.

[2] R. L. Datta and N. Prosad, *ibid.*, 441; *A.*, i, 332.

[3] W. A. Jacobs and M. Heidelberger, *ibid.*, 1435; *A.*, i, 559.

concentrated sulphuric acid by means of aluminium powder has been studied.[4] It has been found that in the electrolytic reduction of aromatic nitro-compounds the yield of aminohydroxy-compounds is increased and that of amino-compounds correspondingly diminished by the use of a cathode of two or more metals. In the case of nitrobenzene, a plain lead cathode gave *p*-aminophenol and aniline in the proportion of about 2 to 3, whilst a copper cathode with lead in the electrolyte gave them in the proportion of 5 or 6 to 1.[5]

Secondary Arylamines.—The preparation and purification of monoalkylated aromatic amines have been investigated. The preparation may be effected by treating the amine with an aliphatic aldehyde in the presence of a reducing agent in a medium not possessing a strongly acid character, when the resulting anhydro-aldehyde-amine, or Schiff base, is simultaneously reduced to the monoalkyl aromatic amine; aniline and formaldehyde thus give methylaniline when reduced with zinc dust and sodium hydroxide.[6] In the preparation of secondary arylamines by the condensation of a primary amine with an alcohol, the product is always contaminated by some unchanged primary amine, which is often difficult to remove owing to the proximity of the boiling points of the two compounds. It has now been found[7] that separation can be effected by heating the mixture with ethyl oxalate and fractionating the product, the primary amine yielding an oxamic ester, $ArNH{\cdot}CO{\cdot}CO_2Et$, of higher boiling point, whilst the secondary amine remains unchanged.

Aryl-substituted Aliphatic Acids.—Several methods for the preparation of these compounds have been described. The condensation products of aromatic aldehydes with diethyl malonate or ethyl cyanoacetate yield on reduction and subsequent hydrolysis aryl-methylmalonic acids which give arylpropionic acids on heating:

$$R{\cdot}CHO + CH_2(CO_2Et)_2 \longrightarrow R{\cdot}CH{:}C(CO_2Et)_2 \longrightarrow R{\cdot}CH_2{\cdot}CH(CO_2H)_2 \longrightarrow R{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$$

Hydroferulic and hydrocaffeic acids have been synthesised in this way.[8]

Substituted naphthylacetic acids have been prepared by two methods. The first is an application of a method previously employed for the preparation of substituted phenylacetic acids,[9] and

[4] A. Eckert and R. Pollak, *Monatsh.*, 1917, **38**, 11; *A.*, i, 345.

[5] Soc. Chem. Ind., Basle, *Brit. Pat.*, 18081 of 1915; from *J. Soc. Chem. Ind.*, 1917, **36**, 129; *A.*, i, 197.

[6] G. T. Morgan, *Brit. Pat.*, 102834; from *J. Soc. Chem. Ind.*, 1917, **36**, 207; *A.*, i, 197.

[7] J. Thomas, *T.*, 1917, **111**, 562; *A.*, i, 451.

[8] A. Lapworth and F. H. Wykes, *ibid.*, 790; *A.*, i, 572.

[9] F. Mauthner, *Annalen*, 1909, **370**, 368; *A.*, 1910, i, 115.

has been used for substituted α-naphthylacetic acids only. For instance, α-naphthaldehyde is condensed with hippuric acid, giving an azlactone, which, on hydrolysis with sodium hydroxide, yields an α-naphthylpyruvic acid, from which α-naphthylacetic acid is

$$C_{10}H_7\cdot CHO + \underset{CO_2H}{CH_2}\cdot NH\cdot COPh \longrightarrow$$

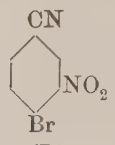
$$C_{10}H_7\cdot CH{:}\underset{CO-O}{C}\cdot N{:}\underset{}{C}Ph \longrightarrow C_{10}H_7\cdot CH_2\cdot CO\cdot CO_2H + NH_3 + Ph\cdot CO_2H,$$

obtained by oxidation.[10] The second method has been applied to the preparation of both α- and β-naphthylacetic acids; these are obtained in yields of 40 to 50 per cent. of the theoretical by a series of reactions which may be represented as follows[11]:

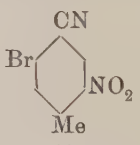
$$R\cdot Me \longrightarrow R\cdot CH_2Br \longrightarrow R\cdot CH_2\cdot CN \longrightarrow R\cdot CH_2\cdot CO_2H.$$

Halogenobenzenes with Mobile Halogen.

It is well known that mobility is conferred on the halogen of a halogenobenzene by two nitro-groups in the *oo*- or *op*-positions, and previous work has shown that one of the nitro-groups may be replaced by other groups, such as the cyano- or benzoyl groups, without preventing the mobility of the halogen. Further study in this field is now recorded, and the test of activity employed is the reaction with ethyl sodiomalonate and ethyl sodioacetoacetate in ethereal suspension. It is shown that one nitro-group alone is not sufficient to render a halogen atom mobile, as, for instance, in *o*-bromonitrobenzene. Of the compounds formulated below, only



(I.)



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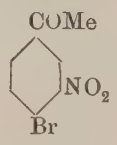
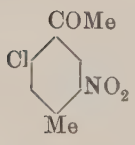
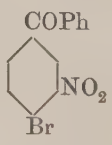


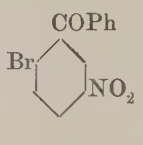
(III.)



(IV.)



(V.)



(VI.)

those numbered (I) to (V) reacted with ethyl sodiomalonate, and only (I) and (III) with ethyl sodioacetoacetate. These facts confirm the previous observation that a nitro-group has a greater influence

[10] F. Mauthner, *J. pr. Chem.*, 1917, [ii], **95**, 55; *A.*, i, 337.

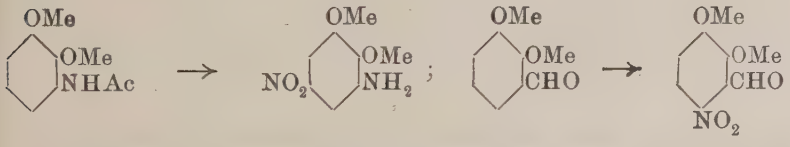
[11] F. Mayer and T. Oppenheimer, *Ber.*, 1916, **49**, 2137; *A.*, 1916, i, 816.

on the mobility of an ortho- than of a para-halogen atom, and it was also found that the cyano-group has a greater effect in conferring mobility than the acetyl residue, whilst both are far superior to the benzoyl residue.[12]

Whilst, however, the mobility of the halogen in the ortho-halogenobenzophenone (VI) was insufficient to answer the particular test employed, yet the benzoyl group alone confers considerable mobility on a halogen atom in the ortho-position, for 2-bromobenzophenone, like benzophenone itself, gives benzhydrol when treated with alcoholic potassium hydroxide, the bromine atom being displaced by hydrogen, whereas the 3- and 4-bromobenzophenones yield 3- and 4-bromobenzhydrols. The fact that 2-bromobenzhydrol is itself stable to alcoholic potassium hydroxide shows that the elimination of bromine precedes the reduction of the ketone, and the mobility of the halogen is due, therefore, to the proximity of the benzoyl substituent.[13]

Alkyl Ethers of Polyhydric Phenols.

The orientating influence of the alkyloxy-groups in catechol ethers has been the subject of several papers.[14] The first substituent invariably takes up a para-position, so that in the case of veratrole only 4-nitro- and 4-bromo-veratrole are obtained. Further treatment then yields a 4:5-disubstituted derivative in nearly every case, but an exception is found in the action of bromine on 4-nitroveratrole, which yields 6-bromo-4-nitroveratrole. With derivatives of veratrole in which a first substituent occupies the ortho-position with respect to a methoxy-group, the orientation of a second substituent is generally influenced by the polarity of the first substituent in the sense that when this is positive it enhances, and when negative counteracts, the influence of the neighbouring methoxy-group. Thus, on nitration, 3-acetylaminoveratrole gives 5-nitro-3-aminoveratrole, but *o*-veratraldehyde gives 6-nitro-*o*-veratraldehyde:

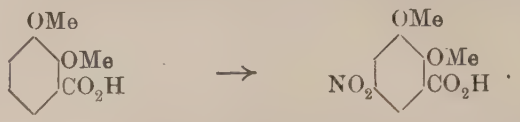


[12] W. Borsche, L. Stackmann, and J. Makaroff-Semljanski, *Ber.*, 1916, **49**, 2222; *A.*, i, 15.

[13] P. J. Montagne, *ibid.*, 2243; *A.*, i, 35.

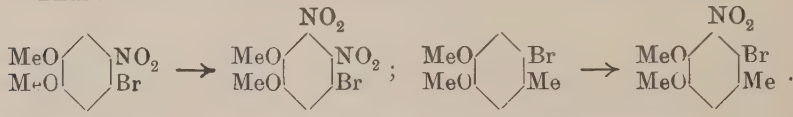
[14] C. S. Gibson, J. L. Simonsen, and M. G. Rau, *T.*, 1917, **111**, 69; *A.*, i, 203; J. L. Simonsen and M. G. Rau, *ibid.*, 220; *A.*, i, 336; T. G. H. Jones and R. Robinson, *ibid.*, 903; *A.*, i, 690.

An exception to this generalisation is found in the behaviour of *o*-veratric acid, which yields 5-nitro-2:3-dimethoxybenzoic acid on nitration:

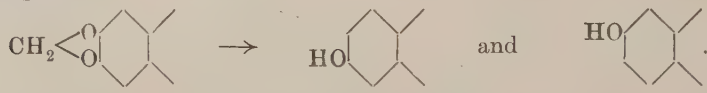


In the preparation of 3:4:5-derivatives from 4:5-disubstituted catechol ethers, the new substituent enters the ortho-position with respect to the more negative of the groups occupying the positions 4 and 5 unless one of these groups is powerfully ortho-directive.

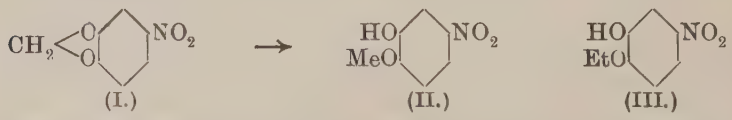
Thus:



Two further observations in this field may be mentioned. The reduction of compounds containing the methylenedioxy-group is known to lead in certain instances to one [15] or both [16] of the possible monophenols:



It is now found [17] that 4-nitrocatechol methylene ether (I) yields 5-nitroguaiacol (II) on treatment with sodium methoxide in methyl-alcoholic solution:



This is not, however, a case of reduction, but of hydrolysis, for the use of sodium ethoxide in ethyl-alcoholic solutions gives a quantitative yield of 5-nitro-2-ethoxyphenol (III).

The second discovery [18] is that halogens, like the nitroxyl group, can replace aldehydo- and carboxyl groups in catechol ethers. Thus piperonylic acid (IV) is converted by the action of bromine in

[15] G. Ciamician and P. Silber, *Ber.*, 1890, **23**, 1162; *A.*, 1890, 965.

[16] F. L. Pyman and F. G. P. Remfry, *T.*, 1912, **101**, 1595.

[17] Mrs. G. M. Robinson and R. Robinson, *ibid.*, 1917, **111**, 929; *A.*, i, 692.

[18] Jones and Robinson, *loc. cit.*; compare also Miss A. M. B. Orr, R. Robinson, and Miss M. M. Williams, *T.*, 1917, **111**, 946; *A.*, i, 703.

aqueous sodium carbonate into 4 : 5 dibromocatechol methylene ether (V), which gives a characteristic colour reaction, and may therefore prove useful in the investigation of acids obtained by the degradation of natural products. The question of the displacement of one group by another—not necessarily in the case of alkyloxy-derivatives—has recently been reviewed in connexion with a study of the displacement of sulphonic acid groups in aminosulphonic acids by halogen atoms.[19] It may be noted here that many phenolic ethers can be demethylated by melting them with aniline hydrochloride.[20]

Dynamic Isomerism.

Two discoveries of general importance in connexion with desmotropic compounds are reported, namely, the influence of soft glass on the melting points of the solid compounds, and the formation of additive compounds with alcohols.

The keto-form of dibenzoylacetylmethane, $CHBz_2{\cdot}CO{\cdot}CH_3$, was previously believed to exist in two forms, melting at 107—110° and 149° respectively, the second form being obtained from the first by heating with acetyl chloride. It is now [21] found that the substance which has not come into contact with alkali melts at 150° in Jena-glass tubes and at 107—110° in soft glass tubes. After washing with dilute sodium acetate, however, it melts at the lower temperature even in Jena-glass tubes; the depression of the melting point in soft glass tubes is therefore due to the alkali of the glass. The fact that after heating with acetyl chloride the substance melts at 150° even in soft glass tubes is explained by the presence in the reagent of chlorides of phosphorus, which leave on evaporation traces of non-volatile acids sufficient to overcome the alkalinity of the glass. The substance melting at 107—110° therefore owes its low melting point to rapid enolisation in the presence of alkali, and is not a distinct variety; consequently, there is no need for the hypothesis put forward by Michael [22] to explain the existence of two stereoisomeric keto-forms of dibenzoylacetylmethane

Earlier observations of the melting points of the enolic form of this compound and of the ketonic and enolic form of tribenzoylmethane are corrected in the light of this discovery, and it is shown [23] in a similar manner that Michael's β-form of ethyl formyl-

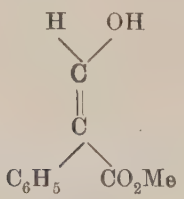
[19] J. J. Sudborough and J. V. Lakhumalani, *T.*, 1917, **111**, 41; *A.*, i, 128.
[20] A. Klemenc, *Ber.*, 1916, **49**, 1371; *A.*, 1916, i, 820.
[21] W. Dieckmann, *ibid.*, 2203; *A.*, 1916, i, 822.
[22] *Ann. Report*, 1912, 124.
[23] W. Dieckmann, *Ber.*, 1916, **49**, 2213; *A.*, 1916, i, 820.

phenylacetate, which Wislicenus[24] regarded as a mixture of the α- and γ-forms, is the γ-form contaminated with traces of alkali.

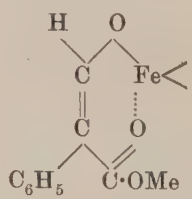
Further light has been thrown on the constitution of the formylphenylacetates by studies of the methyl ester.[25] This occurs in two crystalline forms, the α-form melting at 40—41° and the β-form at 91—93°. Both are apparently enolic, since they combine with bromine readily and completely, and show no difference in their behaviour to dilute alkali. In other respects they differ, the α-form reacting more readily with ferric chloride, copper acetate, and phenylcarbimide, whilst the β-form more readily restores the colour to magenta decolorised by sulphurous acid; the β-form gives no immediate colour reaction with ferric chloride.

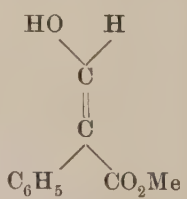
A solution of the β-form in methyl alcohol yields a crystalline additive product, $C_{10}H_{10}O_3 + MeOH$, after keeping for a short time and then cooling with ice and salt, whilst the same additive compound can be isolated from the methyl-alcoholic solution of the α-form only after keeping for a much longer time. It therefore appears that only the β-form is capable of combining with methyl alcohol, and that the formation of the additive product from the α-form is preceded by isomerisation of the α- to the β-form. The additive product does not give a coloration with ferric chloride; it is unstable and readily parts with methyl alcohol, leaving a liquid which gives a deep coloration with ferric chloride and eventually deposits the crystalline α-form.

The ascertained facts have been very fully discussed, but no completely satisfactory interpretation can be given. It is considered most probable that the α- and β-forms are *cis-trans*-isomerides, and that the difference in behaviour towards ferric chloride may be explained by the steric arrangement which permits the formation of co-ordination compounds with the *cis*-form only:



α-Ester.



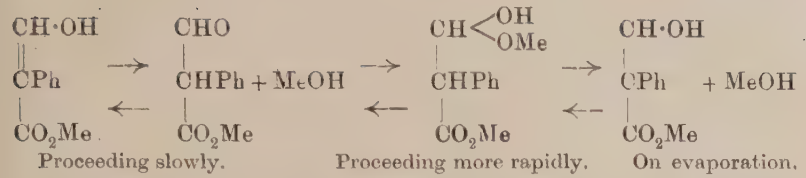


β-Ester.

The formation of the methyl alcohol additive product and its probable condition in methyl-alcoholic solution are represented for the time being by the following scheme:

[24] *Ann. Report*, 1912, 125; see A. Michael, *Annalen*, 1914, **406**, 137; *A.*, 1915, i, 241.

[25] W. Wislicenus and collaborators, *ibid.*, 1916, **413**, 206; *A.*, i, 268; W. Dieckmann, *Ber.*, 1917, **50**, 1375; *A.*, 1918, i, 15.



but it remains to be seen whether or not this view will be modified when more facts come to light and are fully considered. According to a preliminary announcement,[26] methyl oxalacetate, which is enolic in the solid state but mainly non-enolic in alcoholic solution, also forms an additive compound with methyl alcohol; this cannot be represented in the same way as the additive compound with methyl formylphenylacetate, and yet it would appear that the two cases are comparable. It may be noted that the existence of alcoholates of the formylphenylacetates, which was suspected earlier,[27] and has now been established, invalidates many previous explanations of the behaviour of these and other desmotropic compounds in alcoholic solution.

Whilst ethyl oxalacetate has hitherto been isolated in only one solid modification (the enolic), it has been found possible to prepare a substituted derivative of which both the enolic and ketonic modifications are stable.[28] This is diethyl α-oxalo-$\beta\beta$-diphenylpropionate, and here the keto-form is the more stable of the two:

$$\begin{array}{c} CO\cdot CO_2Et \\ | \\ Ph_2CH\cdot CH\cdot CO_2Et \end{array} \qquad \begin{array}{c} C(OH)\cdot CO_2Et \\ \| \\ Ph_2CH\cdot C\cdot CO_2Et \end{array}$$

Other compounds which have been isolated in desmotropic forms are formylnaphthylacetic esters,[29] prepared by the condensation of α- and β-naphthylacetic esters with ethyl formate, and ethyl *o*- and *p*-bromocyanophenylpyruvates, which exist in colourless ketonic and coloured enolic forms, to which the following formulæ are attributed[30]:

$$C_6H_4Br\cdot CH(CN)\cdot CO\cdot CO_2R \qquad C_6H_4Br\cdot C(CN):C(OH)\cdot CO_2R.$$

Colour and Constitution.

In recent papers[31] the coloured additive compounds of quinones and phenols (quinhydrones) and those of aromatic nitro-compounds

[26] W. Wislicenus and K. Eble, *Ber.*, 1917, **50**, 250; *A.*, i, 271.

[27] A. Michael, *Annalen*, 1912, **391**, 275; *A.*, 1912, i, 861; W. Dieckmann, *Ber.*, 1916, **49**, 2213; *A.*, 1916, i, 820.

[28] Wislicenus and Eble, *loc. cit.*

[29] W. Wislicenus and H. Elvert, *Ber.*, 1916, **49**, 2820; *A.*, i, 202.

[30] S. Opolski, L. Czaporowski, and J. Zacharski, *ibid.*, 2283; *A.*, i, 29.

[31] P. Pfeiffer, *Annalen*, 1914, **404**, 1; 1916, **412**, 253; *A.*, 1914, i, 551; 1917, i, 205; J. J. Sudborough, *T.*, 1916, **109**, 1339; *A.*, i, 84.

with aromatic compounds generally, are brought into line with the coloured compounds of ketones with inorganic acids and salts, the colour of which is ascribed by Pfeiffer to halochromy.[32] Compounds of the type of quinhydrones can be obtained from quinones and hexamethylbenzene, and consequently do not depend on the presence of phenolic hydroxyl groups, but rather on an attachment between the carbonyl group and the unsaturated hydrocarbon nucleus, which may be represented as follows:

$$C_6H_6 \ldots O{:}C_6H_4{:}O \ldots C_6H_6.$$

The function of the amino- and phenolic hydroxyl substituents of the benzenoid component of quinhydrones is considered to be auxochromic. Lifschitz, who was previously[33] unable to accept Pfeiffer's views on the constitution of the quinhydrones on account of his experiences in the spectrochemical examination of benzoquinhydrone, now[34] finds that this member is not representative of the class, and accepts Pfeiffer's representation. The compounds of *s*-trinitrobenzene and aromatic compounds are probably of a similar type to the quinhydrones, their formation being due to attachment between the unsaturated nitro-group and the unsaturated hydrocarbon nucleus, $R{\cdot}NO_2 \ldots C_6H_6$. The so-called "picrates" of aromatic hydrocarbons are merely a special case of this type of compound. Confirmation of the above view of the constitution of these compounds is afforded by examination of the additive compounds of *s*-trinitrobenzene.[35] In these, the number of molecules of the nitro-compound with which one molecule of the aromatic compound can combine, does not vary with the number of amino-, substituted amino-, hydroxyl, or alkyloxyl groups present, but rather with the number of aromatic nuclei, the additive compound containing in most cases one molecule of the nitro-compound for each aromatic nucleus. In this connexion, a condensed system of benzene and heterocyclic rings, such as naphthalene and quinoline, has to be regarded as a single nucleus, but compounds such as *s*-diphenylethane and diphenylamine combine with two molecules of the nitro-compound by virtue of their two separate nuclei.

H. Ley[36] has attempted to correlate the degree of unsaturation of certain compounds with their colour. He finds that the absorption spectrum of stilbene is modified by the introduction of a methyl group in the α-position in the direction of the saturated compound dibenzyl. Moreover, stilbene gives a deeper yellow fusion with

[32] Compare *Ann. Report*, 1916, 109.
[33] I. Lifschitz and F. W. Jenner, *Ber.*, 1915, **48**, 1730; *A.*, 1916, i, 45.
[34] I. Lifschitz, *ibid.*, 1916, **49**, 2050; *A.*, 1916, i, 823.
[35] Sudborough, *loc. cit.*
[36] *Ibid.*, 1917, **50**, 243; *A.*, i, 261.

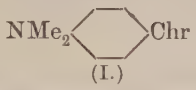
s-trinitrobenzene than α-methyl- or α-phenyl-stilbene, which indicates that stilbene is the most unsaturated of the three compounds, according to Werner's rule that, the more unsaturated the hydrocarbon, the more deeply coloured is the molecular compound.

H. Kauffmann,[37] commenting on this paper, points out many difficulties, and holds that whilst unsaturated character is a factor in the formation of chromophores, it is by no means the factor which determines the degree of chromophoric activity. In contrast to Ley's results, he finds that substitution of an α-hydrogen atom of 2 : 5-dimethoxystilbene by carboxyl or cyano-groups, which are known to increase the degree of saturation of the double linking, actually causes an increase in the colour of the compound:

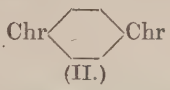
$(MeO)_2C_6H_3\cdot CH{:}CHPh$ (White.) $(MeO)_2C_6H_3\cdot CH{:}CPh\cdot CO_2H$ (Pale greenish-yellow.)

$(MeO)_2C_6H_3\cdot CH{:}CPh(CN)$. (Deep greenish-yellow.)

In another paper, H. Kauffmann[38] gives an account of certain chromophoric groups which have also auxochromic functions. If one considers compounds of the type I and II (where Chr. is the



(I.)



(II.)

chromophoric group), it is seen that (I) contains the strongly auxochromic group NMe_2, which has no chromophoric properties, and consequently behaves normally towards the chromophoric group in the *p*-position without regard to any auxochromic function of the latter; in (II), however, the question as to whether the chromophoric group has auxochromic properties is all-important. If it has not, there is no reason why a compound of this type should be more deeply coloured than the parent compound, $C_6H_5\cdot Chr$, as, for instance, *p*-dinitrobenzene and nitrobenzene, but if the chromophoric groups have auxochromic functions, each acts on the other in the usual way, the effect being to produce a deeper colour than that of the compound $C_6H_5\cdot Chr$. In a case where the styryl radicle is the chromophoric group, *p*-dimethylaminostilbene,

$NMe_2\cdot C_6H_4\cdot CH{:}CHPh$,

is white, whilst *p*-distyrylbenzene, $PhCH{:}CH\cdot C_6H_4\cdot CH{:}CHPh$, is yellow.

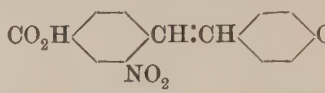
The sodium and potassium salts of ethyl *o*- and *p*-nitrophenylacetate have been isolated[39]; they are all deeply coloured, and presumably have the quinonoid formula,

$EtO\cdot CO\cdot CH{:}C_6H_4{:}NO_2Na(K)$,

[37] *Ibid.*, 630; *A.*, i, 391. [38] *Ibid.*, 515; *A.*, i, 394.
[39] S. Opolski and T. Zwislocki, *ibid.*, 1916, **49**, 1606; *A.*, 1916, i, 815

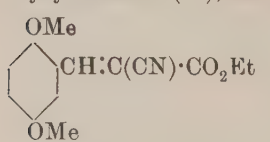
like the salts of *p*-nitrophenylacetonitrile.[40] Coloured salts and esters of *o*- and *m*-nitrophenylacetonitrile have also been prepared [41]; these are of interest in connexion with the question of the existence of meta-quinonoids, for the ortho-, meta-, and para-compounds are so similar that if the ortho- and para-compounds are to be regarded as quinonoids, so also must the meta-compounds.

Chromoisomerism.—In continuation of earlier work,[42] Pfeiffer [43] has published a second paper on the chromoisomerism of the nitromethoxystilbenes, in which it is recorded that only those compounds containing the methoxyl group in the para-position yield chromoisomeric salts. 2-Nitro-4′-methoxystilbene-4-carboxylic acid occurs in a yellow and an orange form. These give orange and

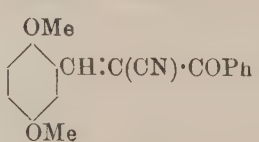


yellow pyridine salts respectively, from which the original varieties of the acid can be recovered by treatment with hydrochloric acid. The orange pyridine salt, however, passes into the yellow salt when treated with excess of pyridine, so that it is possible to pass from the yellow to the orange acid through the pyridine salts, whilst the reverse change can be brought about by heating the orange acid. The two forms of the acid are only capable of existence in the solid form, so that the phenomenon would appear to be that of polymorphism were it not for the fact that each can be converted into the other, as explained above. Elucidation of the constitution of such chromoisomerides will require further work, and in the meantime Pfeiffer regards the subject as being on the border line between polymorphism and chemical isomerism, and terms it 'cryptoisomerism.'

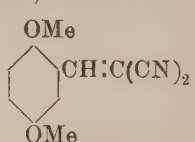
H. Kauffmann [44] has prepared two compounds, ethyl α-cyano-2:5-dimethoxycinnamate (I) and phenyl cyano-2:5-dimethoxystyryl ketone (II), each of which occurs in two forms, which differ



(I.)



(II.)



(III.)

not only in colour but also in the intensity and colour of their fluorescence. A possible explanation that the phenomenon is due

[40] *Ann. Report*, 1916, 110.
[41] S. Opolski, Z. Kowalski, and J. Pilewski, *Ber.*, 1916, **49**, 2276; *A.*, i, 25.
[42] *Ann. Report*, 1916, 108.
[43] *Ber.*, 1916, **49**, 2426; *A.*, i, 140. [44] *Ibid.*, 1324; *A.*, 1916, i, 817.

to *cis-trans*-isomerism is negatived by the fact that 2:5-dimethoxybenzylidenemalononitrile (III) behaves similarly. Another explanation must therefore be sought, and it is suggested that the molecule undergoes changes in internal state other than actual alteration in constitution. The author's views are enunciated as the Principle of Variable States, for further particulars of which the original paper should be consulted.

The Pungent Principles of Ginger.

The results of three independent investigations [45] on the pungent principles of ginger, which have been carried out in this country, the United States of America, and Japan respectively, have been published almost simultaneously. The most important is that of Lapworth and his collaborators, the other two papers covering only part of the ground explored by these authors. The earlier work of Thresh and of Garnett and Grier had shown that the pungent principles were contained in a viscous oleo-resin, "gingerol," from which no crystalline derivatives were obtained. When this substance is methylated by methyl sulphate and alkali, it yields a mixture of an oil with a crystalline compound, termed methylgingerol (Nelson, Lapworth), which is obtained in varying amount according to the purity of the "gingerol," the best yield being 60 per cent. Methylgingerol is decomposed by the action of heat or boiling aqueous alkalis with the formation of methylzingerone, $C_{12}H_{16}O_3$, and aliphatic aldehydes, chiefly *n*-heptaldehyde. When methylzingerone is oxidised by means of aqueous sodium hypobromite, it yields *β*-3:4-dimethoxyphenylpropionic acid (I) and bromoform, which indicates that it is 3:4-dimethoxyphenylethyl methyl ketone (II). This view was confirmed by the synthesis of

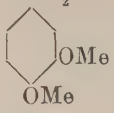
(I) (II.)

the ketone by reduction of veratrylideneacetone (Nomura, Lapworth).

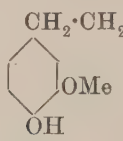
The constitution of methylgingerol is not quite clear, but the compound is probably an aldol-condensation product of *n*-hept-

[45] E. K. Nelson, *J. Amer. Chem. Soc.*, 1917, **39**, 1466; *A.*, i, 572; H. Nomura, *T.*, 1917, **111**, 769; *A.*, i, 570; A. Lapworth, Mrs. L. K. Pearson, and F. A. Royle, *ibid.*, 777; *A.*, i, 571; A. Lapworth and F. H. Wykes, *ibid.*, 790; *A.*, i, 572.

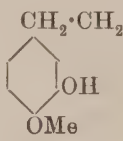
aldehyde and its lower homologues with methylzingerone, and may be represented as follows (Lapworth):



The oleoresin "gingerol" similarly gave a mixture of fatty aldehydes, chiefly *n*-heptaldehyde, and a phenolic ketone, zingerone, $C_{11}H_{14}O_3$, when heated alone or with acids or alkalis. Zingerone gave methylzingerone on methylation, and therefore had one of the formulæ (I) or (II).

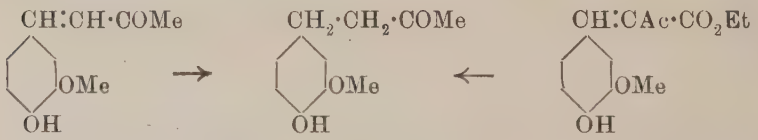


(I.)



(II.)

Its identity with the substance of formula (I) was established synthetically in two ways: (1) by reduction of vanillylideneacetone (Nomura), and (2) by reduction and hydrolysis of ethyl vanillylideneacetoacetate (Lapworth).



So far as the question of the groupings essential to the pungency of gingerol, zingerone, and similar compounds has been investigated, it appears to be certain that the presence of a free phenolic hydroxyl group is necessary, and also probably that of a ketonic carbonyl group suitably disposed in a saturated chain attached to the phenolic residue.

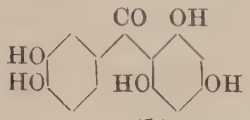
"Paradol," the pungent principle of grains of paradise (*Amomum Melegueta*), behaves like "gingerol" on methylation, giving a mixture of a crystalline substance with an oil, and, it is interesting to note, the crystalline compound has proved to be identical with methylgingerol (Nelson).

Syntheses of Natural Phenolic Ketones.

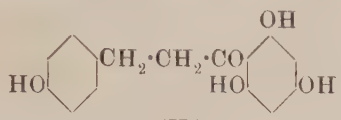
K Hoesch's method [46] for the preparation of phenolic ketones has been successfully applied to the syntheses of maclurin and

[46] *Ann. Report*, 1915, 97.

phloretin. Maclurin is obtained by the condensation of protocatechuonitrile with phloroglucinol,[47] its formulation as 2 : 4 : 6 : 3′ : 4′-pentahydroxybenzophenone (I) being thereby con-



(I.)



(II.)

firmed, whilst phloretin (II) results from the condensation of phloretonitrile (β-*p*-hydroxyphenylpropionitrile) with phloroglucinol.[48]

For the preparation of the nitriles of hydroxybenzoic acids, which are required as starting materials in these condensations, several methods are available. Protocatechuonitrile was first prepared from piperonylonitrile by Ewins,[49] using Barger's method for the hydrolysis of methylene ethers.[50] It may also be obtained by treating protocatechualdoxime with acetic anhydride, when the diacetyl derivative of protocatechuonitrile is obtained, from which the dihydroxy-nitrile can be prepared by careful hydrolysis.[51]

$$(HO)_2C_6H_3\cdot CH{:}N\cdot OH \longrightarrow (AcO)_2C_6H_3\cdot CN \longrightarrow (HO)_2C_6H_3\cdot CN.$$

Phloretonitrile was made by a third method; phloretamide was acetylated to protect the phenolic hydroxyl group, and the acetyl derivative was then dehydrated with phosphoryl chloride, yielding acetylphloretonitrile, from which the acetyl group was removed by mild hydrolysis.[52]

$$AcO\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot CO\cdot NH_2 \longrightarrow AcO\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot CN \longrightarrow HO\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot CN.$$

Ethylene Oxides.

The properties of a group of complex ethylene oxides, obtained by the action of sodium ethoxide on ω-halogenoacetophenones in the presence of an aromatic aldehyde,

$$Ar\cdot CO\cdot CH_2Br + Ar\cdot CHO \longrightarrow Ar\cdot CO\cdot CH\!<\!\begin{matrix}CHAr\\ |\\ O\end{matrix},$$

have been studied, most completely in the case of anisoylphenylethylene oxide, $MeO\cdot C_6H_4\cdot CO\cdot CH\!<\!\begin{matrix}CHPh\\ |\\ O\end{matrix}$, which is obtained from

[47] K. Hoesch and T. von Zarzecki, *Ber.*, 1917, **50**, 462, 660; *A.*, i, 342.
[48] E. Fischer and O. Nouri, *ibid.*, 611; *A.*, i, 393.
[49] T., 1909, **95**, 1488.
[50] Compare *Ann. Report*, 1916, 104.
[51] Hoesch and von Zarzecki, *loc. cit.*
[52] Fischer and Nouri, *loc. cit.*

ω-chloro-*p*-methoxyacetophenone and benzaldehyde.[53] By the addition of the elements of hydrogen chloride, under different conditions, it forms two chlorohydrins,

$MeO{\cdot}C_6H_4{\cdot}CO{\cdot}CHCl{\cdot}CH(OH)Ph$ (I.) $MeO{\cdot}C_6H_4{\cdot}CO{\cdot}CH(OH){\cdot}CHClPh$ (II.),

the constitutions of which follow from the results of treatment with sodium ethoxide, when (I) is reconverted into the ethylene oxide, whilst (II) yields anisyl benzyl diketone.

When anisoylphenylethylene oxide combines with hydroxylamine under varying conditions, it yields three isomeric compounds, all of which lose a molecular proportion of water and give 5-phenyl-3-anisyl*iso*oxazole, $MeO{\cdot}C_6H_4{\cdot}\overset{\overset{\|}{N}\text{---}\overset{|}{O}}{C}{\cdot}CH{:}CPh$, when boiled with acetic acid containing a little concentrated sulphuric acid. Of the three isomerides, two, namely (I*a*) and (II*a*), can be prepared from the chlorohydrins (I) and (II) respectively, and these are formulated as derivatives of 4 : 5-dihydro*iso*oxazole.

$MeO{\cdot}C_6H_4{\cdot}\overset{\overset{\|}{N}\text{---}\overset{|}{O}}{C}{\cdot}CH_2{\cdot}C(OH)Ph$ (I*a*.) $MeO{\cdot}C_6H_4{\cdot}\overset{\overset{\|}{N}\text{---}\overset{|}{O}}{C}{\cdot}CH(OH){\cdot}CHPh$ (II*a*.)

The third isomeride, which appears to be the normal oxime, $MeO{\cdot}C_6H_4{\cdot}C(:NOH){\cdot}CH<\overset{CHPh}{O}$, is transformed by a trace of mineral acid into the compound (II*a*).

Anisoylphenylethylene oxide can be converted by careful treatment with alcoholic sodium hydroxide into the isomeric compound, anisyl ω-hydroxystyryl ketone, $OMe{\cdot}C_6H_4{\cdot}CO{\cdot}C(OH){:}CHPh$, the enolic form of anisyl benzyl diketone, but prolonged treatment with alkalis results in the formation of α-hydroxy-β-phenyl-α-anisylpropionic acid, $MeO{\cdot}C_6H_4{\cdot}C(OH)(CH_2Ph){\cdot}CO_2H$, through the benzil transformation of the diketone first formed.

Phthaleins.

The quantitative decomposition of phenolphthaleinoxime into *o*-4-hydroxybenzoylbenzoic acid and *p*-aminophenol by boiling with dilute sulphuric acid can be explained by assigning the formula (I) to the oxime, and assuming that it undergoes the Beckmann

[53] O. Widman, *Ber.*, 1916, **49**, 477, 2778; *A.*, 1916, i, 406; 1917, i, 221; H. Jörlander, *ibid.*, 2782; 1917, **50**, 406; *A.*, i, 222, 343; S. Bodforss, *ibid.*, 1916, **49**, 2795; *A.*, i, 223.

rearrangement, giving the substance (II), which then suffers hydrolysis.[54] *o*-4-Hydroxybenzoylbenzoic acid is converted quanti-

$$(HO\cdot C_6H_4)_2C<\begin{matrix}N(OH)\\ C_6H_4\text{———}\end{matrix}>CO \longrightarrow$$

(I)

$$HO\cdot C_6H_4\cdot C(OH)<\begin{matrix}N(C_6H_4\cdot OH)\\ C_6H_4\text{———}\end{matrix}>CO \longrightarrow$$

(II.)

$$HO\cdot C_6H_4\cdot CO\cdot C_6H_4\cdot CO_2H + NH_2\cdot C_6H_4\cdot OH$$

tatively into phenolphthalein by heating with phenol, and may well be an intermediate product in the formation of this substance from phenol and phthalic anhydride. It also condenses with other phenols to form mixed phthaleins, as, for instance, with α-naphthol to form α-naphtholphenolphthalein,

$$\begin{matrix}HO\cdot C_6H_4\\ HO\cdot C_{10}H_6\end{matrix}>C<\begin{matrix}C_6H_4\\ O\text{——}\end{matrix}>CO.$$

Hydrocyclic Compounds and Terpenes.

Derivatives of cyclo*Propane.*—The action of different reagents on *cyclo*propane derivatives of the following general formula, where R is hydrogen or an alkyl group, and Ar is an aromatic

$$ArCH^{(2)}\text{—}CH^{(3)}\cdot COAr$$
$$\diagdown\ \diagup$$
$$C(CO_2R)_2$$
$$(1)$$

residue, has been found to result in fission of the *cyclo*propane nucleus in the three possible ways.[55] On reduction with nascent hydrogen, the ring is opened between the 1- and 3-carbon atoms, giving substances of the formula (I), whilst alkalis bring about fission between the 1- and 2-carbon atoms, yielding substances of

$$\begin{matrix}ArCH\cdot CH_2\cdot COAr\\ |\\ CH(CO_2R)_2\end{matrix}\qquad (I)$$

$$\begin{matrix}ArCH{:}C\cdot COAr\\ |\\ CH(CO_2R)_2\end{matrix}\qquad (II.)$$

the formula (II). The addition of hydrogen bromide proceeds in two ways, the ring opening between the 1- and 2-, and also between

[54] W. R. Orndorff and Miss R. R. Murray, *J. Amer. Chem. Soc.*, 1917, **39**, 679; *A.*, i, 339.

[55] E. P. Kohler and J. B. Conant, *ibid.*, 1404, 1699; *A.*, i, 566, 568; E. P. Kohler, G. A. Hill, and L. A. Bigelow, *ibid.*, 2405.

the 2- and 3-carbon atoms, yielding the bromo-acids (III) and (IV), which are very readily transformed into lactonic acids.

$$\underset{\text{(III.)}}{\begin{matrix}\text{ArCHBr·CH·CO·Ar}\\ \quad\quad\text{CH(CO}_2\text{R)}_2\end{matrix}} \qquad \underset{\text{(IV.)}}{\text{ArCHBr·C(CO}_2\text{R)}_2\text{·CH}_2\text{·COAr}}$$

Derivatives of cyclo*Butane*.—Condensation of dialkylacetonedicarboxylates (I) by means of sulphuric acid leads to dialkyl*cyclo*butane-1 : 3-dionecarboxylates (II), which readily suffer fission

$$\underset{\text{(I.)}}{\begin{matrix}\text{EtO·CO·CHMe·CO}\\ \quad\quad\quad\text{EtO·CO·CHMe}\end{matrix}} \longrightarrow \underset{\text{(II.)}}{\begin{matrix}\text{EtO·CO·CMe·CO}\\ \quad\quad\quad\text{CO—CHMe}\end{matrix}}$$

when boiled with water, or when treated with hydrazine, hydroxylamine, or aniline, yielding derivatives of dialkylacetonedicarboxylates.

Treatment of dialkyl*cyclo*butanedionecarboxylates with alkyl haloids and sodium ethoxide in alcoholic solution leads—presumably through unstable trialkyl*cyclo*butanedionecarboxylates (III)—to trialkylacetonedicarboxylates (IV). When heated with

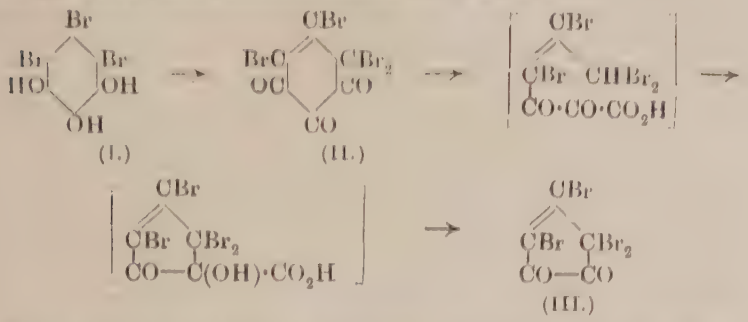
$$\text{(II.)} \longrightarrow \underset{\text{(III.)}}{\left[\begin{matrix}\text{EtO·CO·CMe·CO}\\ \quad\quad\quad\text{CO—CMeEt}\end{matrix}\right]} \longrightarrow \underset{\text{(IV.)}}{\begin{matrix}\text{EtO·CO·CHMe·CO}\\ \quad\quad\quad\text{EtO·CO·CMeEt}\end{matrix}}$$

aqueous baryta, the dialkyl*cyclo*butanedionecarboxylates yield dialkyl*cyclo*butane-1 : 3-diones, $\text{R·CH}\!<\!\begin{matrix}\text{CO}\\ \text{CO}\end{matrix}\!>\!\text{CHR}$. These differ in many important respects from dimeric ketenes, which cannot therefore be derivatives of *cyclo*butane-1 : 3-diones, as was believed previously.[56]

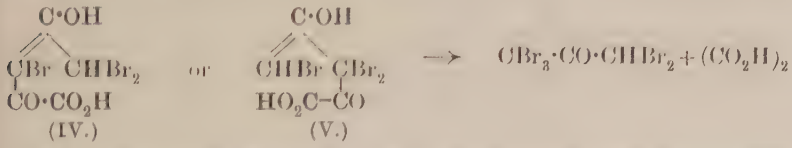
Xanthogallol, a Derivative of cyclo*Pentene*.—Xanthogallol was discovered by Stenhouse,[57] who prepared it by the action of bromine and water on tribromopyrogallol, and assigned to it the formula $C_{18}H_4O_6Br_{14}$. This empirical formula was confirmed later by Theurer,[58] who proposed for the substance a structural formula involving three reduced benzene rings connected by oxygen atoms. Recently, the substance and its reactions have been thoroughly investigated by F. J. Moore and Miss R. M. Thomas,[59] who have shown, by analysis, that xanthogallol contains no hydrogen, and has the formula $C_5O_2Br_4$, confirmed by determination of the molecular weight. They consider it to be a *cyclo*pentene derivative

[56] G. Schroeter, *Ber.*, 1916, **49**, 2697; *A.*, i, 145.
[57] *Journ. Chem. Soc.*, 1875, **28**, 1.
[58] *Annalen*, 1888, **245**, 327; *A.*, 1888, 1084.
[59] *J. Amer. Chem. Soc.*, 1917, **39**, 974; *A.*, i, 460.

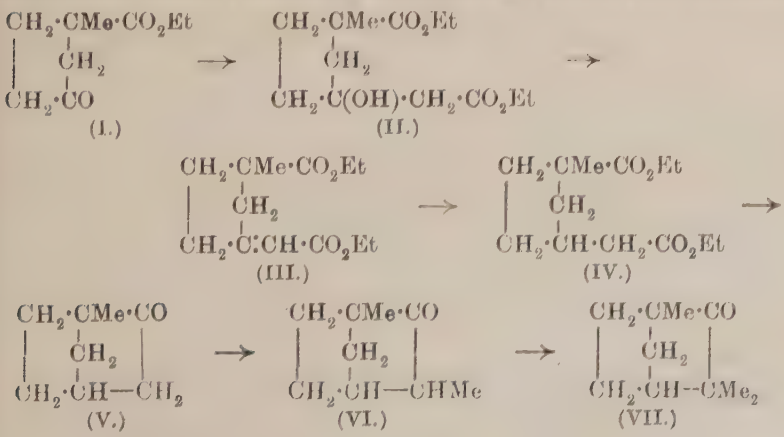
(III), and interpret its formation from tribromopyrogallol (I) through tetrabromo*cyclo*hexenetrione (II) as follows:



This formula satisfactorily explains the fact that xanthogallol forms a quinoxaline derivative, and yields on treatment with sodium hydroxide a compound, xanthotonic acid (IV or V), which is converted smoothly by bromine water into pentabromoacetone and oxalic acid.



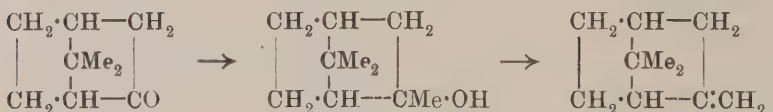
The Synthesis of Fenchone.—L. Ruzička [60] has effected the complete synthesis of *r*-fenchone, and thus confirmed Semmler's formula for this ketone. Ethyl 1-methyl*cyclo*pentan-4-one-1-carboxylate (I) was condensed with ethyl bromoacetate, and water was eliminated from the resulting compound (II), giving ethyl dehydro



[60] *Ber.*, 1917, **50**, 1362; *A*, 1918, i, 22.

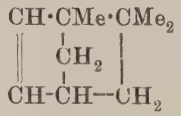
methylnorhomocamphorate (III). By reduction, ethyl methylnorhomocamphorate (IV) was formed, the lead salt of which gave methylnorcamphor (V) on distillation. This was treated twice with methyl iodide and sodamide, when a mixture of fenchosantenone (VI) and fenchone (VII) resulted.

Fenchenes.—G. Komppa and R. H. Roschier[61] propose an alteration in the nomenclature of fenchenes. They employ the terms α- and β-fenchenes, using the former for the substance which yields the hydroxyfenchenic acid and fenchocamphorone of higher melting point. Wallach's *Dl*-fenchene is therefore *l*-α-fenchene, and his *Dd*-fenchene is *d*-β-fenchene. They have completed the synthesis of *r*-α-fenchene (III)[62] by preparing it from *r*-α-fenchocamphorone (I), which had been synthesised previously,[63] and find that *r*-α-fenchene is identical with *iso*pinene. The synthesis was effected by the action of magnesium methyl iodide on *r*-α-fenchocamphorone and distillation of the resulting alcohol (II) under atmospheric pressure, when water was eliminated.



(I.) (II.) (III.)

It has been proposed[64] that terpenes which retain the original fenchane ring system, and thus differ from the fenchenes, shall be called fenchylenes; a fenchylene (IV) has been prepared by the



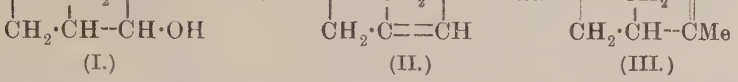
(IV.)

distillation of methyl *iso*fenchylxanthate.

Santene.—The hydrocarbon obtained by the removal of hydrogen chloride from camphenilyl chloride was previously termed camphenilene. It now proves to be a mixture, and can also be prepared by the dehydration of camphenilol (I) by sodium hydrogen sulphate at 200°. The main constituent of the mixture is a hydrocarbon identical with santene (III), and it is proposed to retain

[61] *Acad. Sci. Fennicae*, 1915, [*A*], **7**, 1; *A.*, i, 398.
[62] G. Komppa and R. H. Roschier, *ibid.*, 1916, [*A*], **10**, 3; *A.*, i, 466.
[63] *Ann. Report*, 1914, 120.
[64] S. S. Nametkin and Mlle. A. K. Rushenceva, *J. Russ. Phys. Chem. Soc.* 1916, **48**, 450; *A.*, i, 152.

the term camphenilene for the constituent (II) present in smaller quantity.[65]



(I.) (II.) (III.)

The complete synthesis of santene has now been effected, for camphenilone, from which camphenilol is obtained, was synthesised previously.[66]

Cholesterol.

A. Windaus[67] has now achieved by chemical means a reaction which hitherto has been effected only in the living organism, namely, the reduction of cholesterol to coprosterol. Whilst the hydrogenation of cholesterol in the presence of platinum yields β-cholestanol,[68] the use of nickel at 200° gives rise to a new product, γ-cholestanol, which has the same melting point and specific rotatory power as β-cholestanol, but differs from it in crystallising from dilute alcohol without water of crystallisation. γ-Cholestanol has proved to be an additive compound (partial racemate) of β-cholestanol (about 50 per cent.), ψ-coprosterol (δ-cholestanol), and ε-cholestanol. The β-variety was removed by precipitation with digitonin, but the other two could not be separated directly. Advantage was therefore taken of the fact that on boiling with amyl alcohol and sodium amyloxide, ε-cholestanol is converted into β-cholestanol to the extent of about 90 per cent., whilst ψ-coprosterol is only converted into coprosterol to the extent of about 10 per cent. After treatment of the mixture of ε-cholestanol and ψ-coprosterol in this way, the β-cholestanol and coprosterol were removed by precipitation with digitonin, when the filtrate contained ψ-coprosterol contaminated with only a small amount of ε-cholestanol, and after a repetition of the treatment the first was obtained practically free from its isomerides. Finally, the ψ-coprosterol was converted into the equilibrium-mixture containing about 20 per cent. of coprosterol by the action of sodium ethoxide at 180°. The mixture was treated with digitonin, when

[65] G. Komppa and S. V. Hintikka, *Bull. Soc. chim.*, 1917, [iv], **21**, 13; *A.*, i, 214.

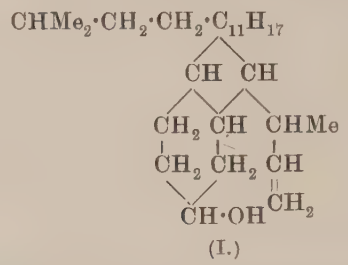
[66] G. Komppa and S. V. Hintikka, *Ber.*, 1914, **47**, 1550; *A.*, 1914, i, 852.

[67] *Ibid.*, 1916, **49**, 1724; *A.*, 1916, i, 813.

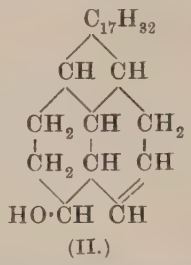
[68] Consult *Ann. Report*, 1916, 119, for the relations between the reduction products of cholesterol, and for their partial formulæ.

the compound of digitonin and coprosterol separated, from which coprosterol was recovered by extraction with boiling xylene.

It appeared recently[69] that Windaus had modified his partial formula for cholesterol, the formula (I) being replaced by (II).

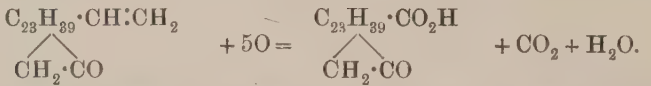


(I.)

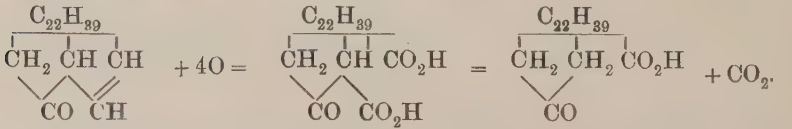


(II.)

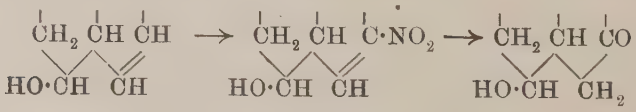
The reasons for this modification have since been published,[70] and are as follows. The keto-carboxylic acid obtained by the oxidation of cholestenone was previously believed to have the formula $C_{26}H_{42}O_3$, and to be formed in accordance with the equation below:



A large number of analyses have now shown that it contains two more atoms of hydrogen, and should be formulated $C_{26}H_{44}O_3$. It cannot therefore be formed from cholestenone by the oxidation of a vinyl group, and is now represented as resulting from the fission of an unsaturated ring, in the following manner:



Support for the new formula is found in the previously known fact that the unsaturated nitro-cholesterol can be converted readily into a keto-alcohol, cholestanonol, in which the keto-group is contained in a fully hydrogenised ring. This reaction is now represented as follows:



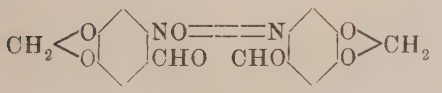
[69] *Ann. Report*, 1916, 119.

[70] A. Windaus, *Ber.*, 1917, **50**, 133; *A.*, i, 265.

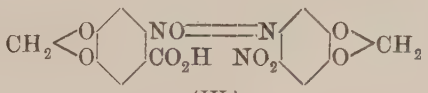
Aromatic Compounds of Nitrogen.

Azoxy-compounds.—The unsymmetrical formulation of azoxybenzene as $PhNO{:}NPh$[71] is supported by the behaviour of azoxyveratrole (I) and azoxypiperonal (III) on nitration, for whilst compounds containing two veratrole nuclei symmetrically placed, for example, diveratrylmethane and azoveratrole, do not yield mononitro-derivatives, but give symmetrical dinitro-derivatives as first products, azoxyveratrole yields a mononitro-derivative (II), whilst azoxypiperonal gives an unsymmetrical nitrocarboxylic acid (IV).[72]

(I.) (II.)



(III.)

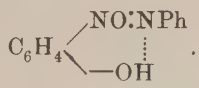


(IV.)

In the case of *o*-hydroxyazoxybenzene, which has long been known to occur in two forms, the simple explanation that these are to be formulated as (V) and (VI) is not completely satisfactory. It does not explain why one form is readily soluble in dilute

$HO{\cdot}C_6H_4{\cdot}N{:}NOPh$ (V.) $HO{\cdot}C_6H_4{\cdot}NO{:}NPh$ (VI.)

alkalis, is easily oxidised by alkaline permanganate, and dyes silk and wool, whilst the other (*iso*) form lacks these properties. O. Baudisch[73] now suggests that whilst the more active form has the formula (V), the *iso*-form may be represented by the formula



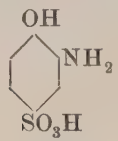
An azoxy-compound has been obtained by the oxidation of phenylazocarbonamide with hydrogen peroxide,

$$PhN{:}N{\cdot}CO{\cdot}NH_2 \longrightarrow PhNO{:}N{\cdot}CO{\cdot}NH_2.$$

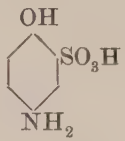
[71] *Ann. Report*, 1916, 122.
[72] Mrs. G. M. Robinson, *T.*, 1917, **111**, 109; *A.*, i, 226.
[73] *Ber.*, 1917, **50**, 333; *A.*, i, 356.

Hot aqueous acids or alkalis decompose it, with the production of the transformation products of diazobenzene.[74]

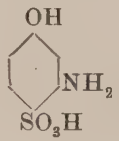
Diazophenols.—The nature of the anhydrides formed by the diazotisation of aminophenolsulphonic acids has recently been investigated.[75] On diazotisation, *o*- and *p*-aminophenols give coloured diazo-oxides, whilst aminosulphonic acids give colourless anhydrides, such as the well-known "diazobenzenesulphonic acid," and there are therefore two possible alternatives for the course of the reaction with aminophenolsulphonic acids. Three such acids were diazotised, namely, *o*-aminophenol-4-sulphonic acid (I), *p*-aminophenol-2-sulphonic acid (II), and *m*-aminophenol-4-sulphonic acid (III).



(I.)

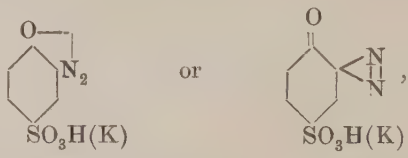


(II.)

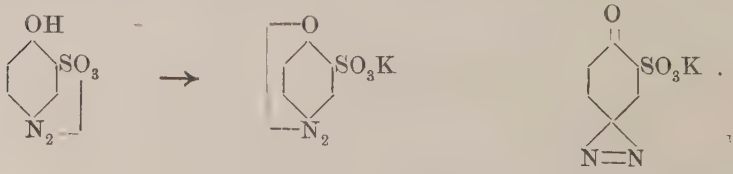


(III.)

The first gave a yellow anhydride, and the colour of its aqueous solution was not appreciably altered by the addition of aqueous alkalis, whence it appears that the free anhydride and its alkali salts have the same chemical constitution; this anhydride is therefore an *o*-diazo-oxide or *o*-quinonediazide.[76]



p-Aminophenol-2-sulphonic acid gives a colourless diazo-derivative, which forms yellow alkali salts. The colour change indicates a change in constitution from internal diazonium-sulphonate to *p*-diazo-oxide or *p*-diazoquinone.



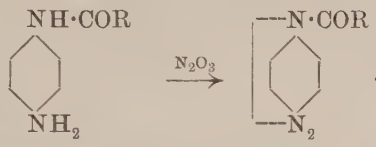
[74] A. Angeli, *Atti R. Accad. Lincei*, 1917, [v], **26**, i, 95, 207; *A.*, i, 228, 417.

[75] G. T. Morgan and H. P. Tomlins, *T.*, 1917, **111**, 497; *A.*, i, 481.

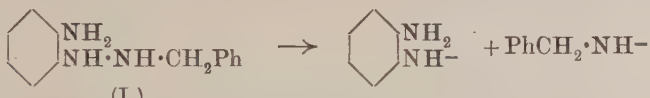
[76] For previous work on the comparative merits of the possible alternative formulæ of internal diazo-oxides, see *Ann. Report*, 1915, 114.

The diazo-derivative of *m*-aminophenol-4-sulphonic acid is a colourless internal diazonium-sulphonate, and on treatment with alkali decomposes and shows no tendency to form a meta-diazo-oxide—a type of compound which does not appear to exist.

An advance has also been made in the investigation of the allied diazoimides by the preparation of the hitherto inaccessible acyl derivatives of *p*-diazoiminobenzene, by diazotising acyl-*p*-phenylenediamines with liquid nitrous anhydride in dry acetone.[77]



Fission of Hydrazines.—A study of the properties of *o*-amino-*β*-benzylphenylhydrazine has led H. Franzen and B. von Fürst[78] to express views on the mode of decomposition of substituted hydrazobenzenes. By heating at 120—130°, *o*-amino-*β*-benzylphenylhydrazine (I) is converted into benzaldehyde-*o*-aminophenylhydrazone (III), benzylamine, and *o*-phenylenediamine. This reaction is explained by the assumption that the hydrazine is first dissociated into two unsaturated residues, which are then reduced



(I.)

by a second molecule of the hydrazine. This thereby becomes oxidised to an azo-compound (II), which suffers rearrangement to the isomeric benzaldehyde-*o*-aminophenylhydrazone. The whole

(II.) (III.)

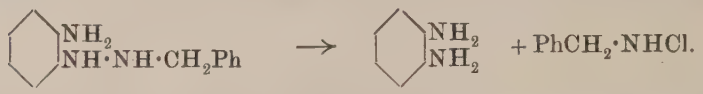
course of the decomposition is similar to the spontaneous change of hydrazobenzene into a mixture of azobenzene and aniline, which the authors interpret in the same way,

$$2PhNH\cdot NHPh \longrightarrow 2PhNH- + PhNH\cdot NHPh \longrightarrow 2PhNH_2 + PhN{:}NPh,$$

holding, contrary to the view of Wieland,[79] that there is no reason why diphenylhydrazines should not be supposed to dissociate into free radicles, as do the tetraphenylhydrazines.

[77] G. T. Morgan and A. W. H. Upton, *T.*, 1917, **111**, 187; *A.*, i, 300.
[78] *Annalen*, 1916, **412**, 14; *A.*, i, 58.
[79] *Ann. Report*, 1915, 113.

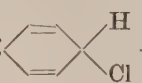
When *o*-amino-β-benzylphenylhydrazine is heated with dilute hydrochloric acid, it undergoes a series of transformations, which are best explained by the assumption that hydrogen chloride is added at the N–N linking with the formation of *o*-phenylenediamine and benzylchloroamine, and it is pointed out that a similar

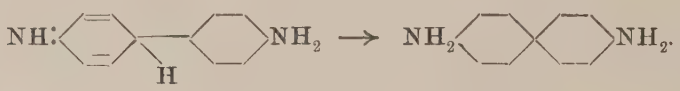


assumption in the case of substituted hydrazobenzenes affords an explanation of the formation of azo- and amino-compounds, and of the benzidine and semidine transformations.

1. $PhNH\cdot NHPh + HCl \longrightarrow PhNH_2 + PhNHCl.$

2. (*a*) $PhNHCl + PhNH\cdot NHPh \longrightarrow PhNH_2,HCl + PhN{:}NPh.$

(*b*) $PhNHCl \longrightarrow$  $+ PhNH_2 \longrightarrow$



(*c*) $PhNHCl + PhNH_2 \longrightarrow PhNH\cdot C_6H_4\cdot NH_2.$

Autoxidation of Hydrazones.—The autoxidation of benzaldehydephenylhydrazone in alcoholic solution yields a complicated mixture of products from which diphenyldibenzylidenehydrotetrazone, $PhCH{:}N\cdot NPh\cdot NPh\cdot N{:}CHPh$, benzaldehyde, and benzoic acid were previously isolated.[80] A more detailed examination [81] of the course of the reaction and the components of the product has given interesting results. If the autoxidation is carried out in indifferent solvents, such as hydrocarbons, benzaldehydephenylhydrazone peroxide can be isolated. This substance is unstable, and is readily converted into benzoylphenylhydrazine and benzoylazobenzene.

When the autoxidation takes place in alcoholic solution, the peroxide cannot be isolated, but benzoylphenylhydrazine and compounds presumably derived from benzoylazobenzene are found. Thus, the formation of benzoyldiphenylbenzylidenehydrotetrazone

[80] H. Stobbe and R. Nowak. *Ber.*, 1913, **46**, 2887; *A.*, 1913, i, 1200.

[81] M. Busch and W. Dietz, *ibid.*, 1914, **47**, 3277; *A.*, 1915, i, 307; M. Busch and H. Kunder, *ibid.*, 1916, **49**, 2345; *A.*, i, 56.

may be explained by the addition of benzoylazobenzene to the unchanged hydrazone.

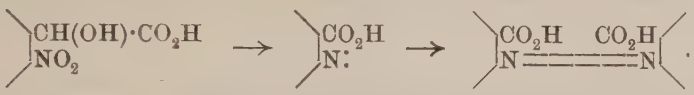
$$PhCO{\cdot}N{:}NPh + PhNH{\cdot}N{:}CHPh \longrightarrow PhCO{\cdot}NH{\cdot}NPh{\cdot}NPh{\cdot}N{:}CHPh.$$

Another constituent of the mixture, benzoylphenylhydrazinobenzaldehydephenylhydrazone, $PhCO{\cdot}NH{\cdot}NPh{\cdot}CPh{:}N{\cdot}NHPh$, is derived from this hydrotetrazone, from which it may be prepared by keeping in alcoholic acetic acid solution. Other substances isolated were benzeneazodiphenylmethane and its isomerisation product, benzophenonephenylhydrazone,

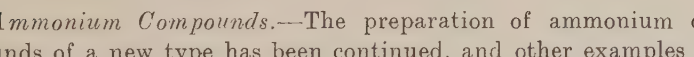
$$NPh{:}N{\cdot}CHPh_2 \longrightarrow NHPh{\cdot}N{:}CPh_2,$$

besides the three compounds which had been identified previously.

Intramolecular Change.—Simultaneous oxidation and reduction within the molecule bring about the conversion of substituted *o*-nitromandelic acids into derivatives of 2 : 2′-azobenzoic acid:



This reaction, which was first observed on heating 6-nitro-3 : 4-methylenedioxymandelic acid with nitrobenzene,[82] can also be brought about by the action of hot aqueous alkali hydroxides on the acid, but in this case about a quarter of the acid is converted into the azoxy-compound.[83] Other substituted *o*-nitromandelic acids undergo the same change—for instance, 6-nitro-3 : 4-dimethoxymandelic acid[84] and 6-chloro-2-nitromandelic acid.[85] The transformation resembles that effected by the action of hot aqueous alkalis on derivatives of *p*-nitrotoluene, when azoxystilbenes are formed, together with nitroso- and azo-stilbenes.[86]



Ammonium Compounds.—The preparation of ammonium compounds of a new type has been continued, and other examples may be added to that of triphenylmethyltetramethylammonium, $CPh_3{\cdot}NMe_4$.[87] Instances are benzyltetramethylammonium,

$$PhCH_2{\cdot}NMe_4,$$

[82] Mrs. G. M. Robinson and R. Robinson, *T.*, 1914, **105**, 1466; 1915, **107**, 1753; *A.*, 1916, i, 166.

[83] Mrs. G. M. Robinson, *ibid.*, 1917, **111**, 109; *A.*, i, 226.

[84] Mrs. G. M. Robinson and R. Robinson, *loc. cit.*

[85] S. Reich and W. Merki, *Bull. Soc. chim.*, 1917, [iv], **21**, 8; *A.*, i, 227.

[86] F. Bender and G. Schultz, *Ber.*, 1886, **19**, 3234; *A.*, 1887, 268; P. Karrer, *ibid.*, 1915, **48**, 305; *A.*, 1915, i, 333.

[87] *Ann. Report*, 1916, 111; W. Schlenk and J. Holtz, *Ber.*, 1917, **50**, 262, 274, 276; *A.*, i, 255, 262.

and di-*p*-tolylaminotetramethylammonium, $(C_7H_7)_2N{\cdot}NMe_4$, which are obtained by the action of tetramethylammonium chloride on sodium benzyl and potassio-di-*p*-tolylamine respectively. Sodium benzyl is itself new, and is obtained by the action of sodium on mercury dibenzyl. It is a red, crystalline compound which inflames in the air. It is ionised in ethereal solution; this indicates that the metallic atom is linked by a carbonium valence, as in the case of sodium triphenylmethyl, which it resembles closely.

Organo-metallic Compounds.

Lead.—The synthesis of lead tetra-alkyls containing four different primary alkyl groups has now been achieved. Mixed lead tetra-alkyls, containing only primary alkyl groups, when treated with halogens at $-75°$, yield lead trialkyl haloids with the loss of one alkyl group, which is invariably the smallest of those present. Thus, lead trimethylethyl yields lead dimethylethyl haloids, which on treatment with magnesium *n*-propyl haloids give lead dimethylethyl-*n*-propyl. By a similar series of operations, this is converted successively into lead methylethyl-*n*-propyl haloid and finally into lead methylethyl-*n*-propyl-*n*-butyl.[88]

Lead tetra-alkyls containing secondary alkyl groups, however, behave differently, the secondary alkyl groups being less firmly attached to the lead atom than the primary radicles. Thus, lead tetra*iso*propyl loses two alkyl groups when treated with halogen at $-75°$, giving lead di*iso*propyl dihaloids, and lead diethyldi*iso*propyl yields lead diethyl dihaloids.[89] In the case of the lead tetra-primary-alkyls, treatment with halogen at a higher temperature, $-20°$, is necessary to remove two alkyl groups, and the lead dialkyl dihaloids so formed are then stable towards halogen at the ordinary temperature.[90] When these dihaloids are treated with magnesium alkyl haloids, mixed lead tetra-alkyls of the type $PbR_2R'_2$ are obtained; thus, lead tetramethyl can be converted through lead dimethyl dichloride into lead dimethyldiethyl.[91]

Another method of preparing the same compound is as follows: lead tetraphenyl yields with bromine lead diphenyl dibromide, from which lead diphenyldiethyl is obtained by Grignard's reaction; on treatment with hydrogen bromide, this yields lead diethyl dibromide, which reacts with magnesium methyl iodide to give lead dimethyldiethyl.[92] Halogen hydrides can also be employed

[88] G. Grüttner and E. Krause, *Ber.*, 1917, **50**, 202; *A.*, i, 256.
[89] *Ibid.*, 574; *A.*, i, 384.
[90] *Ibid.*, 1916, **49**, 1415; *A.*, 1916, i, 799.
[91] *Ibid.*, 1546; *A.*, 1916, i, 800.
[92] S. Möller and P. Pfeiffer, *ibid.*, 2441; *A.*, i, 122.

to prepare lead trialkyl haloids from lead tetra-alkyls, and the lead trialkyl haloids when treated with silver hydroxide in aqueous solution give alkaline solutions of lead trialkyl hydroxides, from which other salts may be prepared by neutralisation with acids.[93]

FRANK LEE PYMAN.

PART III.—HETEROCYCLIC DIVISION.

A FEW words of explanation are necessary in order to define the scope of this section of the Reports. Year by year, with the duration of the war, the regular circulation of foreign journals has been more and more interrupted until, in the past eighteen months, it has been difficult to procure any recent Continental periodicals within a reasonable time after their publication. Thus some of the journals for 1916 did not come to hand until the present year, and when it became necessary to draw up this Report, it was found that several important papers had escaped notice in the 1916 volume, to which they properly belonged. In these circumstances, it seemed best to include them in the present Report rather than allow them to pass without reference. The Reporter is aware that this decision to some extent oversteps the limits set him, but he believes that the reader's judgment in the matter will coincide with his own.

The section headings of the Report give an idea of its contents, so it is scarcely necessary to expatiate on the various subjects in this place. Mention, however, may be made of the new synthesis of tropinone and also of the important paper on the natural synthesis of alkaloids. Hitherto, it has been assumed by Guareschi and Pictet that alkaloids are formed in the plant as a result of degradation, and not by direct synthesis from simpler compounds; but Robinson has now indicated methods whereby the direct synthesis might be attained in simple ways, and it appears, from his own synthesis of tropinone, that these methods are not merely theoretical, but may be achieved in practice.

New Heterocyclic Types.

Last year, mention was made of some new heterocyclic rings in which elements hitherto unknown in that guise played their parts

[93] P. Pfeiffer, P. Truskier, and P. Disselkamp, *Ber*., 1916, **49**, 2445; *A*., i, 122.

as members of the cyclic system.[1] Further details are now available with regard to some lead derivatives.[2]

By the interaction of lead diethyl dichloride and the magnesium compound of αε-dibromopentane, diethyl*cyclo*pentamethyleneplumbine has been isolated:

$$CH_2<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}>Pb<\begin{matrix}C_2H_5\\C_2H_5\end{matrix}.$$

This substance, when treated with bromine, yields lead diethyl-ε-bromoamyl bromide, a compound which appears to react abnormally, since with magnesium ethyl bromide it yields lead diethyl-ε-bromoamyl, the reactive halogen atom being left unaffected in the end-product.

The cyclic lead compound also is abnormal, in that it is oxidised in the air, and it is suggested that this variation from the usual stability of tetra-alkyl lead derivatives should be ascribed to the tension in the ring. The argument may be sound, but there seems no reason why a six-membered ring should not be reasonably stable, if one may judge from analogy to carbon compounds. Possibly some other factor lies at the root of the matter.

Sozoiodol–Mercury Compounds.

The majority of the organic compounds of mercury which are employed in pharmacy may be divided into two classes. In the first group lie those substances which contain mercury in the ionisable form, such as mercury salts of organic acids; whilst the second set comprises compounds in which the mercury is not in an ionisable condition, but is attached directly to the organic nucleus. It is found that some of these compounds are insoluble in water, but are capable of being dissolved by a solution of sodium chloride. There is no great difficulty in accounting for this phenomenon in the case of the two classes just mentioned. In the case of the organic salts of mercury, double decomposition is assumed to take place between the mercury salt and the sodium chloride, with the formation of a sodium salt and mercuric chloride, which then dissolve in the water present. With regard to the substances containing organically combined mercury, it is assumed that they form sodium salts of chloromercuri-aromatic acids by the addition of sodium chloride, and that these new compounds are soluble in water.

[1] *Ann. Report*, 1916, 131.

[2] G. Grüttner and E. Krause, *Ber.*, 1916, **49**, 2666; *A.*, i, 122.

An inspection of the formula of sozoiodol–mercury,

$$C_6H_2I_2\langle^{-O-}_{SO_3}\rangle Hg,$$

shows that it belongs to neither of the classes already mentioned. It is not a mercury salt of the ordinary type, nor is its mercury atom held to the nucleus by linking it with a carbon atom. None the less, it is soluble in a solution of sodium chloride.

Sozoiodol–mercury is prepared[3] (1) by the action of yellow mercuric oxide on sozoiodolic acid (2 : 6-di-iodophenolsulphonic acid); (2) by the interaction of mercuric nitrate and sodium sozoiodolate; or (3) by adding a warm aqueous solution of sodium sozoiodolate to an equivalent amount of mercuric acetate solution.

When a solution of sozoiodol–mercury in aqueous solution is extracted with ether, mercuric chloride is removed in a proportion which indicates that the following equation probably represents the interaction between sozoiodol–mercury and sodium chloride:

$$C_6H_2I_2\langle^{-O-}_{SO_3}\rangle Hg + 2NaCl = HgCl_2 + NaO{\cdot}C_6H_2I_2{\cdot}SO_3Na.$$

It appears, therefore, that sozoiodol–mercury behaves analogously to ordinary organic salts of mercury.

A second problem is suggested by sozoiodol–mercury. It contains only two chromophoric groups in the ordinary sense—the iodine atoms—although the benzene ring might also be regarded as a possible third. None the less, it is orange in colour. From the results given in the paper under review, it appears possible that the group ·O·Hg·O· possesses a chromophoric character.

Cyclic Sulphides.

A complete group of sulphides has been examined containing four-, five-, six-, and seven-membered rings, one member of each ring being a sulphur atom.[4] The compounds were synthesised by the action of sodium sulphide on the appropriate dihalogen derivative of a paraffin, wherein the two halogen atoms are attached to opposite ends of the chain. In most cases, the product contains a mixture of substances, namely, the unimolecular sulphide, a polymerised sulphide, and a third product, which is probably a dihalogenated thio-ether. In the case of the four-membered ring, the yield is small.

All these sulphides behave like open-chain sulphides on oxidation, sulphones being formed on oxidising them with permanganate.

[3] E. Rupp and A. Herrmann, *Arch. Pharm.*, 1916, **254**, 488; *A.*, i, 516.

[4] E. Grischkevitsch-Trochimovski, *J. Russ. Phys. Chem. Soc.*, 1916, **48**, 880, 901, 928, 944, 951, 959; *A.*, i, 153–158.

With methyl iodide, trimethylene sulphide forms a peculiar methiodide having the composition $C_3H_6S,2MeI$, in which both the iodine atoms are precipitable with silver nitrate. The six- and seven-membered sulphides form the ordinary type of additive product, having one molecule of methyl iodide attached to the sulphide. All the sulphides unite with mercuric chloride, giving compounds of the type $R,HgCl_2$, where R represents one molecule of the sulphide.

As a class, the new sulphides are colourless, mobile liquids with unpleasant odour; they distil undecomposed, are insoluble in water, but soluble in ordinary organic solvents. Chemically, they are akin to the aliphatic thio-ethers. They do not react with benzoyl chloride, alkalis, or sodium. With bromine, they form very unstable additive compounds.

Owing to the fact that diethylene disulphide methiodide shows a certain parallelism with the methiodides of tertiary cyclic imines, it was thought that analogous results of exhaustive methylation might be expected in the case of the methiodides of the new cyclic sulphides,

$$\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}\!\!>\!NMe_2I \xrightarrow{-HI} CH_2{:}CH\cdot CH_2\cdot CH_2\cdot NMe_2$$

$$S\!<\!\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}\!\!>\!SMeI \xrightarrow{-HI} CH_2{:}CH\cdot S\cdot CH_2\cdot CH_2\cdot SMe$$

but it was found that there are exceptions to the general reaction. When heated with potassium hydroxide solution, 2-methyltetrahydrothiophen methiodide behaves in accordance with anticipation, yielding an open-chain sulphide:

$$\begin{matrix}CH_2\cdot CHMe\\ CH_2\text{---}CH_2\end{matrix}\!\!>\!SMeI \xrightarrow{KOH} \begin{matrix}CH_2\cdot CHMe\\ CH_2\text{---}CH_2\end{matrix}\!\!>\!SMe\cdot OH$$

$$\downarrow$$

$$HO\cdot CHMe\cdot CH_2\cdot CH_2\cdot CH_2\cdot SMe$$

$$\downarrow -H_2O$$

$$CHMe{:}CH\cdot CH_2\cdot CH_2\cdot S\cdot Me$$

Similar treatment of pentamethylene sulphide methiodide, however, simply results in the regeneration of the parent pentamethylene sulphide, no opening of the ring taking place. On the other hand, 2-methylpentamethylene sulphide methiodide gives an open-chain sulphide in the normal manner.

With regard to physical properties, the new sulphides show abnormality in their refractive indices. If the refraction constant for the sulphur atom is calculated by subtracting the normal values for the carbon and hydrogen atoms from the total refractivity of the molecule, it is found that the figure thus obtained is very close indeed to the value for sulphur in the thiophen series, instead of approximating, as might be expected, to the value for sulphur in the alkyl sulphides. This, combined with other abnormal properties, suggests that these new sulphides will form an interesting field of research; there must be some reason for the approximation of refractive power of the sulphur atoms in the sulphides and the thiophen series, although in the one case there is an atom incapable of manifesting any increase of valency, whilst in the case of the sulphides the sulphur atoms can show quadri- and even sexavalency.

The Thiophen Series.

In the Annual Report for 1914[5] it was mentioned that the action of mercuric chloride on thiophen gives rise to both mono- and di-mercurichlorides. This reaction has now[6] been extended, and proves to be a means of preparing other compounds of interest.

When thiophen mercurichloride is treated with two molecules of sodium iodide, the product of the reaction is found to be mercury dithienyl in almost quantitative yield:

$$2C_4H_3S,HgCl + 4NaI = Hg(C_4H_3S)_2 + 2NaCl + HgI_2,2NaI.$$

By substituting for thiophen mercurichloride other analogous compounds, a whole series of mercury derivatives of thiophen has been prepared. All these substances behave similarly when treated with mercuric haloids in acetone solution, regenerating the original thiophen mercurihaloid derivative. Thus the parent substance, mercury dithienyl, regenerates thiophen mercurichloride in accordance with the following equation:

$$Hg(C_4H_3S)_2 + HgCl_2 = 2C_4H_3S,HgCl.$$

The only exception hitherto observed in this series is the substance 2:5-dimethylthiophen-3-mercurichloride, which remains unchanged when an attempt is made to bring it into reaction with sodium iodide. It is suggested that if this abnormal behaviour of compounds with mercury in the β-position proves to be general, it will furnish a simple method of distinguishing the α- and β-derivatives from each other.

[5] P. 128.

[6] W. Steinkopf and M. Bauermeister, *Annalen*, 1917, **413**, 310; *A.*, i, 302

By utilising the interaction of thiophen mercurichloride or mercury diethienyl with arsenic trichloride, it has been found possible to prepare arsenic derivatives of thiophen. Thus when arsenic trichloride is shaken with powdered mercury dithienyl, a mixture of three thiophen arsenic derivatives is obtained: thienylchloroarsine, $C_4H_3S\cdot AsCl_2$; dithienylchloroarsine, $(C_4H_3S)_2AsCl$; and trithienylarsine, $(C_4H_3S)_3As$.

A new and simple method of preparing thienyl ketones[7] has been worked out, based on Lecher's method of synthesising the aromatic ketones. Thiophen, mixed with about 2 per cent. by weight of phosphoric oxide, is allowed to react with acetyl chloride at 98—130°, and the product contains a 52 per cent. yield of 2-acetothienone. Other acid chlorides give corresponding thiophen ketones. The reaction is supposed to take place in the following three stages when an acid anhydride is used:

(1) $P_2O_5 + 2Ac_2O = 2PO_2\cdot OAc$.
(2) $PO_2\cdot OAc + C_4H_3S = C_4H_3S\cdot COMe + PO_2\cdot OH$.
(3) $PO_2\cdot OH + PO_2\cdot OAc = P_2O_5 + CH_3\cdot CO_2H$.

When an acid chloride is substituted for an anhydride, the first stage is modified into

(1*a*) $P_2O_5 + CH_3\cdot COCl = PO_2\cdot OAc + PO_2Cl$,

and the third stage becomes

(3*a*) $PO_2\cdot OH + PO_2Cl = P_2O_5 + HCl$.

One special advantage of the reaction in the thiophen series as compared with the benzene derivatives lies in the fact that much lower temperatures are required in the former group in order to carry through the process.

Pyrrole and its Derivatives.

Among the numerous types of heterocyclic compounds, the derivatives of pyrrole appear to rank high as a class which furnishes a starting point for varied and numerous researches. In 1914, the production of alkylated pyrroles by different methods occupied investigators; in 1915, the centre of interest was transferred to the polymerisations of pyrrole compounds; whilst in the earlier part of 1916 the main line of research tended towards the study of the action of oxidising agents on members of the pyrrole group.

[7] W. Steinkopf, *Annalen*, 1917, **413**, 343; *A.*, i, 278.

During the latter part of the year, however, a fresh field was found in the condensation of pyrrole with various ketones and aldehydes.[8]

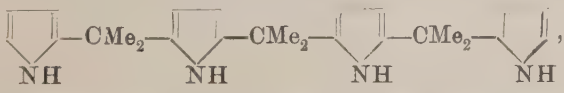
Four main products of the condensation of pyrrole with acetone have been isolated, namely, (1) a crystalline substance, $C_{28}H_{36}N_4$; (2) an amorphous substance, $C_{28}H_{36}ON_4$; (3) a non-crystalline substance, $C_{25}H_{32}N_4$; and (4) a crystalline compound, $(C_{28}H_{36}ON_4)_3$. When the condensation is carried out in acetone solution, (1) and (2) are obtained in almost equal proportions. In alcoholic solution at the ordinary temperature, the results are similar, but in hot alcoholic solution the end-product is almost entirely the compound (1). In aqueous solution at the ordinary temperature, the compound (1) still makes its appearance, but the main bulk of the product is the substance (3). In presence of mineral or common organic acids, the reaction yields compound (1) as before, but, in addition, compound (4) makes its appearance.

The compound (3) appears to be formed by a simple condensation reaction between four molecules of pyrrole and three molecules of acetone:

$$4C_4H_5N + 3COMe_2 = C_{25}H_{32}N_4 + 3H_2O.$$

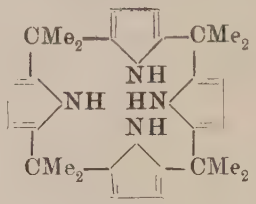
It is therefore referred to as the "tetrapyrrole–triacetone" derivative. On heating with hydrochloric acid in presence of acetone, it is converted almost entirely into the compound (1), which is therefore termed the "tetrapyrrole–tetra-acetone" derivative. Compound (1) is also formed when the compound (4) is heated with hydrochloric acid.

Compounds (1) and (3) are evidently related to etioporphorin, since on oxidation they yield maleinimide, whereas etioporphorin itself when oxidised gives a substituted maleinimide. From the volume of gas evolved when (1) and (3) are treated with magnesium propyl iodide, it has been deduced that the four imino-groups of the pyrrole residues are still intact, and the products of this reaction show a behaviour similar to that of carbamic acids. From the production of unsubstituted maleinimide from (1) and (3) by oxidation, it is safe to argue that, in the condensation reaction by which they are formed, no attack has been made at positions 3 and 4 of the pyrrole ring. This limits the problem to condensation at position 2, and from certain facts observed in connexion with the distillation of the compound (1), it has been assumed that (3) has the structure shown below:



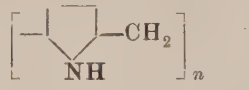
[8] V. V. Tschelincev and B. V. Tronov, *J. Russ. Phys. Chem. Soc.*, 1916, **48**, 105; 127, 1197; *A.*, i, 91, 93, 411; Tschelincev, Tronov, and S. G Karmanov, *ibid.*, 1210; *A.*, i, 412.

whilst compound (1) is supposed to have the following formula, which recalls Küster's formula for hæmin:

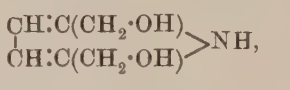


A further series of investigations has been carried out involving the condensation of pyrrole with other ketones, the results being analogous to those detailed above.

Substitution of formaldehyde for acetone and the use of acid condensing agents[9] produces a compound which appears to have the structure (I), and when the condensation is carried out in



(I.)



(II.)

presence of potassium carbonate, the product is a glycol, 2:5-dimethylolpyrrole (II), which, on oxidation, produces pyrrole-2:5-dicarboxylic acid, so that the reaction forms a method of preparing acids of this type.

The new method of methylating pyrrolidyl *iso*propyl alcohol mentioned in last year's Report[10] has been extended to other substances, and has been shown to be a general reaction.[11] Thus α-2-pyrrolidylbutyl alcohol when heated with formic acid and 40 per cent. formaldehyde solution at 105—110° in a sealed tube is converted into α-1-methyl-2-pyrrolidylbutyl alcohol.

Pyridine and Piperidine.

Less attention than usual has been paid to this class during the current year. When the sodium compound of pyridine, C_5H_5NNa, is treated with moist ether, a mixture of tetrahydropyridyls is formed,[12] and from the fact that autoxidation of the mixture yields 2:2′-dipyridyl and 4:4′-dipyridyl, it may be assumed that the tetrahydro-compounds are similarly constituted.

In the Annual Report for 1914,[13] attention was directed to the

[9] V. V. Tschelincev and B. V. Maksorov, *J. Russ. Phys. Chem. Soc.*, 1916, **48**, 748, 779; *A.*, i, 164–5.

[10] *Ann. Report*, 1916, 141.

[11] K. Hess, C. Uibrig and A. Eichel, *Ber.*, 1917, **50**, 344; *A.*, i, 351.

[12] B. Emmert, *ibid.*, 31; *A.*, i, 221.

[13] P. 146.

use of pyridine as a solvent and reagent, and the current year has brought to light some additional examples[14] of its utilisation in this branch of the subject. Thus when thiocarbamide is boiled in pyridine solution, it is converted into guanidine thiocyanate and a compound which is regarded as ammonium trithiocarbonate.

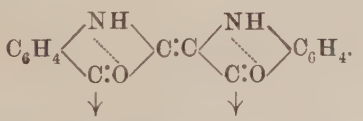
Similar treatment converts thioaminophenol into diaminophenyl sulphide,

$$2SH\cdot C_6H_4\cdot NH_2 \longrightarrow H_2S + S(C_6H_4\cdot NH_2)_2,$$

whilst thioacetanilide, in pyridine contaminated with water, produces acetanilide and hydrogen sulphide. Piperidine appears to have properties similar to those of pyridine in the capacity for removing hydrogen sulphide from compounds.

The Indole Group.

A study of the absorption spectra of various derivatives of indigotin has been carried out,[15] and it has been found that marked alterations are observed when sulphuric acid is substituted for a solvent compounded of chloroform and stannic chloride. The colour changes observed in the indigotin series closely resemble those found in the case of the halochromic $\alpha\beta$-unsaturated ketones, which also change their tint in presence of acids. In order to account for the optical data obtained, it is suggested that the formula for indigotin should be written thus:

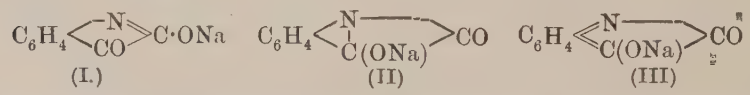


It must be frankly confessed that a formula of this type suggests but little to the ordinary chemist, and it seems doubtful whether much is gained by the use of such schemes. In recent times there has been a good deal of this kind of thing, and many authors seem to imagine that they have "explained" the occurrence of colour merely by putting a few dotted lines into their formulæ. Even if we suppose that such partial valencies exist in molecules, their mere occurrence does not give us any idea of the origin of colour in the compounds represented. The introduction of an arrow and a dotted line into the indigotin formula can scarcely be regarded as a step towards the explanation of the physical origin of the tint of the substance itself. Residual affinity and the occurrence of colour often can be proved to co-exist, but unless we get some clear physical

[14] M. Raffo and O. Balduzzi, *Gazzetta*, 1917, **47**, i, 65; *A.*, i, 382.
[15] I. Lifschitz and H. Lourié, *Ber.*, 1917, **50**, 897; *A.*, i, 586.

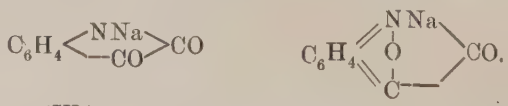
idea connecting the two phenomena, progress is likely to be slow. In many cases, it looks as if the art of formula-mongering had become an end in itself, divorced altogether from any idea of the physical side of the subject.

Heller[16] has suggested that the various salts of isatin and its ethers and oximes owe their differences of colour mainly to the different mode of attachment of the metallic atoms to the nucleus, and he states that the N-salts are deeper in tint than the O-salts. Claasz,[17] on the other hand, criticises this view adversely. He bases his objection on the fact that no N- or C-metallic salts are known in which the metallic atom is not removed by solution in water; and yet, none the less, isatin gives a blue salt which, owing to its dissolving unchanged in water, can only be an O-salt. Claasz points out that isatin gives three O-salts, to which he ascribes the following formulæ.



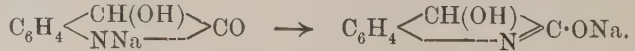
(I.) (II) (III)

The structure (II) corresponds with the red salt of the red isomeride of isatin discovered by Heller[16] (see below); formula (III) represents a blue salt, soluble in water, and its enhanced colour leads to the quinonoid structure being applied to it. The deep blue *N*-sodium salt of isatin changes to red on solution in water, owing to its conversion into an *O*-salt. It would scarcely be safe to ascribe the blue tint solely to the *N*-attachment of the metallic atom, since there is a blue *O*-salt known also, the colour of which could not be accounted for on this basis. Heller has suggested that its structure should be represented by (IV), but Claasz objects to this on the ground of insufficient chromophores, and proposes instead the formula (V) with the quinonoid structure:



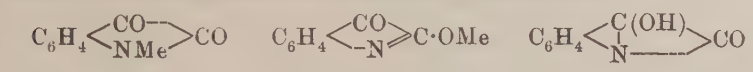
(IV.) (V.)

Heller[18] has applied his views to the case of the dioxindole sodium salts, one of which is violet, whilst the other is colourless. He ascribes this colour change to the transformation of the *N*-salt into the *O*-salt, as shown below:



[16] G. Heller, *Ber.*, 1916, **49**, 2757; *A.*, i, 219.
[17] M. Claasz, *ibid.*, 1917, **50**, 511; *A.*, i, 413.
[18] G. Heller and H. Heine, *ibid.*, 1916, **49**, 2775; *A.*, i, 220.

An interesting case of isomerism has been detected in the isatins.[19] The lactam and lactim ethers of isatin (corresponding with the formulæ *A* and *B* below) have long been known, but isatin itself was found only in one form, the second desmotropic possibility not having been realised in practice. This gap in our knowledge has now been filled by the discovery of an isomeride of isatin, termed isatol, to which the structure *C* is ascribed.

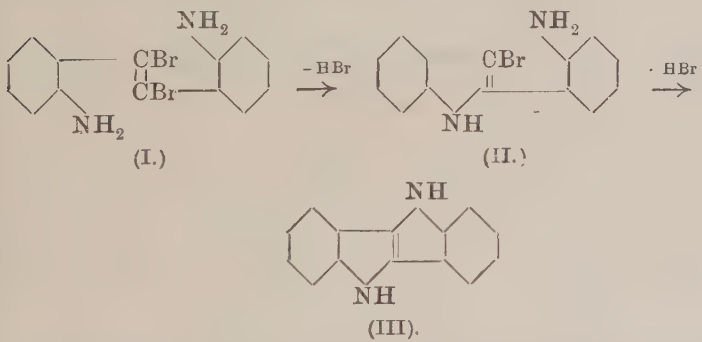


A. *B.* *C.*

Isatol is prepared by acting on the N-silver salt of isatin with benzoyl chloride and benzene, silver chloride being formed and isatol being liberated. It is a red, crystalline substance which is insoluble in ammonia, whereas isatin is soluble.

A Doubly Condensed Indole.

A new type of derivative of the indole group[20] has been obtained by a double application of Lipp's indole synthesis. The stages in the process are shown by the formulæ below:



(I.) (II.)

(III).

The substance (I) is prepared from $\alpha\alpha$-dibromo-2 : 2′-dinitrostilbene by reduction with stannous chloride dissolved in a solution of hydrogen chloride in glacial acetic acid. The conversion of (I) into (II) takes place by boiling for a short time with alcoholic picric acid, and the second stage of the condensation is attained by prolonged boiling of (II) with alcoholic potassium hydroxide. The compound (III), for which the name "dindole" is proposed (a contraction of di-indole), is very pale yellow. Condensed nuclei of this type are known in the pyrrole group, but this appears to be the first example of such a structure in the indoles.

[19] G. Heller, *Ber.*, 1916, **49**, 2757; *A.*, i, 219.

[20] P. Ruggli, *ibid.*, 1917, **50**, 883; *A.*, i, 586.

The Relative Stability of Cyclic Bases in the Hofmann Reaction.

The Hofmann reaction referred to in the title of this section may perhaps be more easily recognised under the title of "exhaustive methylation," and is used to indicate the reaction by means of which an unsaturated tertiary open-chain base is derived from a cyclic quaternary ammonium hydroxide by the elimination of water. The experiments[21] which have recently been carried out in this field show that the elimination of water is not a necessary part of the reaction, as hydroxy-amines are frequently formed.

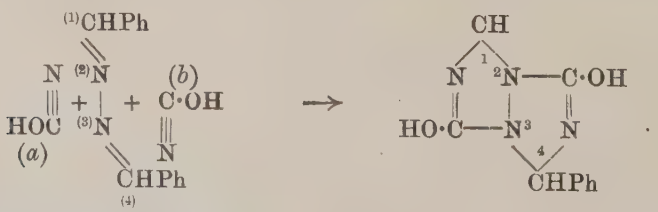
When various cyclic bases are submitted to the reaction, and the amount of decomposition in each case is estimated from an examination of the end-products, it is found that the stability of the ring increases in the following order: tetrahydro*iso*quinoline, dihydro*iso*indole, pyrrolidine, piperidine, dihydroindole, and tetrahydroquinoline.

Another reaction which causes fission in these cyclic systems is found in the application of cyanogen bromide on the molecules in question. Curiously enough, in this case also the order of stability is almost exactly the same as that given in the last paragraph.

Since the two reactions are so very different from each other, it is suggested that the stability of the cyclic system in such cases is intimately connected with the nature of the forces at work in the molecule as a whole.

Criss-cross Addition to Conjugated Systems.

In glacial acetic acid solution, benzaldazine readily takes up two molecules of cyanic acid, forming 5 : 3′-dihydroxy-3 : 5′-diphenyldihydro-1 : 2-triazolotriazole:

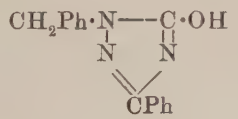


An examination of the formulæ will make it clear that the additive reaction has taken place in what may be termed an abnormal manner. From analogy to other reactions of conjugated double bonds, it might have been expected that one molecule of cyanic acid would attach itself to the positions 1 and 4 of the benzaldazine

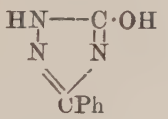
[21] J. von Braun, *Ber.*, 1916, **49**, 2629; *A.*, i, 169.

chain, leaving the second molecule to fix itself in positions 2 and 3. Actually what occurs is that one molecule of cyanic acid attacks positions 1 and 3, whilst the other attaches itself at 2 and 4, a process which may conveniently be described as "criss-cross" addition.[22] Two factors seem to militate against the possibility of the normal action of the conjugated system in this case. In the first place, addition of cyanic acid in the positions 1 and 3 would entail the formation of a new bond between two carbon atoms, whereas the actual course of the reaction permits the formation of the new ring by means of linked carbon and nitrogen, which is a much more common additive reaction. Secondly, the actual course of the reaction ends in the production of two five-membered rings, which are usually marked by stability, whereas if the addition took place at the positions 1, 4, and 2, 3 the substance produced would contain one six-membered and one four-membered ring, a much less stable type. It seems probable that these two factors give the key to this apparently abnormal behaviour of the conjugated system. The point is of interest, and if there are any new cases of the kind detected in future it may serve to throw light on the still very obscure problem of unsaturation.

When the triazolotriazole is dissolved in 10 per cent. aqueous potassium hydroxide and subjected to steam distillation, part of it is converted into a compound which appears to have the structure (I); whereas when oxidised with concentrated nitric acid below 10° it yields (II):



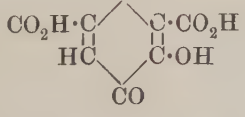
(I.)



(II.)

The Constitution of Meconic Acid.

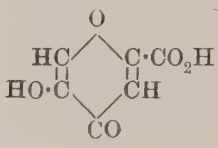
An attempt[23] has been made to establish the constitution of meconic acid, which has hitherto been regarded as the trihydrate of 3-hydroxy-4-pyrone-2 : 6-dicarboxylic acid:



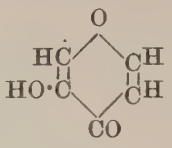
[22] J. R. Bailey and N. H. Moore, *J. Amer. Chem. Soc.*, 1917, **39**, 279; *A.*, i, 355; J. R. Bailey and A. T. McPherson, *ibid.*, 1322; *A.*, i, 587.

[23] W. Borsche, *Ber.*, 1916, **49**, 2538; *A.*, i, 117.

It is now shown that on reduction by means of hydrogen in presence of colloidal palladium it yields $\alpha\beta\gamma\epsilon$-tetrahydroxypimelic acid, $CO_2H{\cdot}CH(OH){\cdot}CH(OH){\cdot}CH(OH){\cdot}CH_2{\cdot}CH(OH){\cdot}CO_2H$. Now



(I.)



(II.)

when comenic acid (I) and pyromeconic acid (II) are reduced, the pyrone bridge is not broken and the end-products of the reactions are pentamethylene oxide derivatives. The conclusion is drawn that meconic acid is not constituted analogously to comenic and pyromeconic acids, and that instead of being a true pyrone derivative it is really an open-chain compound of the following constitution: $CO_2H{\cdot}C(OH)_2{\cdot}CH(OH){\cdot}CO{\cdot}CH_2{\cdot}C(OH)_2{\cdot}CO_2H$. Bearing in mind the difference in constitution between the various compounds assumed to be analogous, the evidence may be taken for what it is worth. The presence of two hydroxyl radicles attached to a single carbon atom in the grouping $\cdot CH_2{\cdot}C(OH)_2{\cdot}CO_2H$ appears to be scarcely in accordance with experience.

The Mechanism of Pseudo-base Condensation.

In connexion with some reactions of berberine derivatives, a new theory of the reactions between pseudo-bases and pseudo-acids has been suggested by Mrs. G. M. Robinson and R. Robinson.[24] When a dilute aqueous acetic acid solution of cotarnine is mixed with nitromethane and sodium acetate is added, the product of the reaction is anhydrocotarninenitromethane. Now cotarnine, under the conditions of the experiment, may be supposed to contain either of the groups (I) and (II), the former being the carbinolamine form whilst the latter represents an unsaturated ammonium hydroxide.

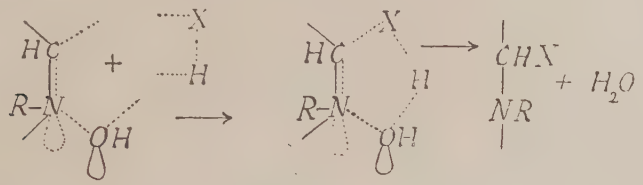
$\cdot CH(OH){\cdot}NMe\cdot$	$\cdot CH{:}NMe(OH)\cdot$
(I).	(II.)

From a survey of the evidence at their disposal, the authors conclude that (II) represents the reactive form of this part of the cotarnine chain. Originally,[25] the suggestion was made that the reactions of such substances could best be expressed as a result of the interactions of ions; but this view is now displaced by the hypothesis of a simple addition. The ionic hypothesis when applied

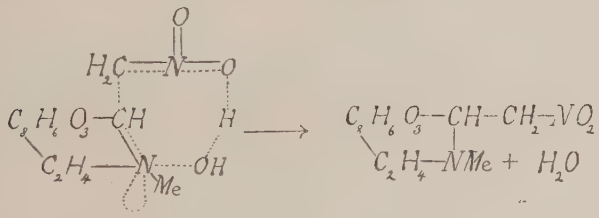
[24] Mrs. G. M. Robinson and R. Robinson, *T.*, 1917, **111**, 958; *A.*, i, 706.
[25] E. Hope and R. Robinson, *ibid.*, 1911, **99**, 2119.

to the reaction between a pseudo-acid and a pseudo-base, demanded the assumption of two intramolecular changes, which are dispensed with in the later suggestion.

Applying the addition hypothesis to a general case, the following scheme results:



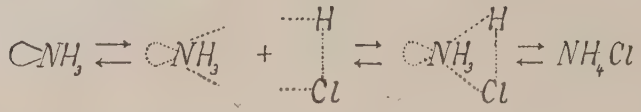
It will be seen that on the left we have the two reagents coming within each other's reaction-sphere, and that each reagent is assumed to display certain partial valencies. In the second phase of the reaction, a complex is formed which is held together by the partial valencies. In the final stage of the reaction, rupture of the original bond between H and X occurs, accompanied by the elimination of water. The second and third stages of the cotarnine–nitromethane reaction mentioned above are shown in the scheme below:



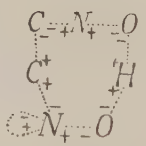
In order that these changes may be clearly understood, it is necessary to point out that a further assumption with regard to partial valency is made in those cases where disruption of a molecule results from the reaction. The case of the formation of ammonium chloride will make the matter clear. In the first place, when a pair of partial valencies is assumed to exist in a molecule, the valency utilised in forming the partial valencies is supposed to be derived from the normal valencies of the molecule; and hence these normal valencies become weakened. Thus hydrogen chloride displaying no partial valency would be represented with a full valency bond between the atoms; whilst when the partial valencies are called into play, the bond between the atom is weakened and is to be represented by a dotted line:

H——Cl ...H...Cl...

The formation of ammonium chloride would therefore be expressed by the following scheme:



A final point must be indicated. When a normal valency is weakened in order to provide two partial valencies, the two parts will have the same polarity, being either positive or negative; whereas when a *latent* valency (such as exists in tervalent nitrogen) gives rise to two partial valencies these will be of opposite signs. Applying this to the scheme given above for the interaction of nitromethane and cotarnine, it will be found that the polarity of the partial valencies engaged in the ring-formation (complex-formation) is representable according to the following arrangement:



This theory has been applied to other organic reactions, such as the bromination of ketones and the mechanism of diazo-coupling; but the reader may be left to trace its full development for himself in the original paper.

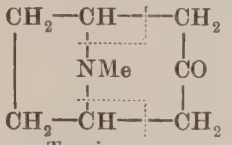
A New Synthesis of Tropinone.

The drawbacks of the classical method of alkaloidal synthesis are apparent to anyone. Starting, often, with out-of-the-way materials which themselves are obtainable only with considerable difficulty (suberone in the Willstätter synthesis of tropine, for example), the alkaloidal skeleton is built up laboriously by adding group to group and chain to chain until the structure is complete. In favour of this method it may be adduced that it places beyond doubt the constitution of the finished product; and from this point of view the step-by-step mode of synthesis will always retain its value. From two other points of view, however, it is deficient in many cases. It is often expensive, and therefore its products cannot compete with the natural alkaloid in commerce; and, further, it throws little light on the methods whereby plants carry out their synthetic processes which result in the formation of the alkaloid class.

Entirely fresh ground has been broken by a novel synthesis of

tropinone,[26] for the new method appears on the one hand capable of yielding a cheap product, whilst on the other it holds out the hope that we are at last on the track of natural synthetic processes.

An examination of the formula of tropinone shows that it exhibits a marked symmetry of structure; and if the structure be imagined as disrupted at the dotted lines, it becomes evident that it consists of a succinyl radicle, a methylamine nucleus, and an acetone group:



Tropinone.

Following this line of thought, succindialdehyde, acetone, and methylamine were allowed to interact in aqueous solution for half-an hour, at the end of which tropinone was found to be present in the mixture. As a test for tropinone, the dipiperonylidene derivative was used, which is readily formed when piperonal acts on tropinone.

Modifications of the above method of synthesis have also been found successful. In one of them ethyl acetonedicarboxylate is substituted for acetone; in another, the calcium salt of acetone-dicarboxylic acid is used. By the latter method no less than a 42 per cent. yield was obtained of tropinone, calculated on the weight of succindialdehyde employed.

It will be seen that this new method of synthesis opens up a very wide field owing to its simplicity and the good return for the material employed; and it marks a great advance on the older methods of preparation.

A Theory of Alkaloidal Synthesis in Plants.

The mechanism by means of which certain plants are able to synthesise the complicated structures of the alkaloidal type has hitherto baffled the ingenuity of most chemists. It is self-evident that the processes employed in our laboratories are not akin to those employed in the natural formation of the alkaloid class; for the plant is forced to work within a very limited range of temperature, and the reagents at its disposal can scarcely be assumed to compete in variety with those of the investigator. Clearly, then, the natural processes must be of a simple nature; they must be capable of acting at the ordinary temperature and they must not demand complicated reagents for their work.

[26] R. Robinson, *T.*, 1917, **111**, 762; *A.*, i, 581.

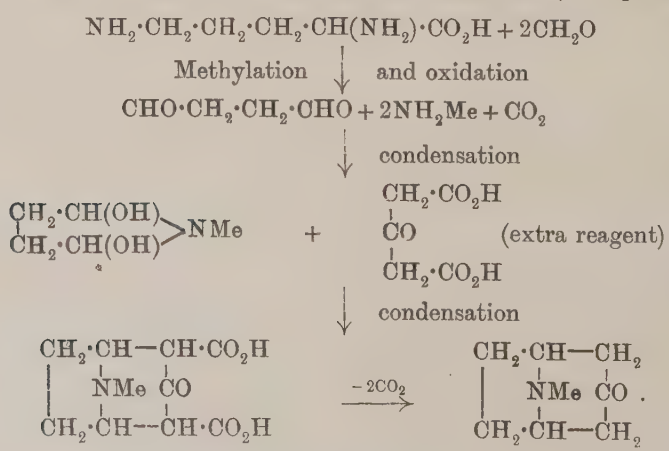
Robinson[27] has put forward a series of suggestions as to the manner in which many of the familiar alkaloidal skeletons may be produced in the course of comparatively simple reactions, and his paper should be studied by all who are interested in the problem. Unfortunately, its ingenuity would lose by condensation, so that only the barest outline of it can be indicated in this place. Examples are given of possible lines of synthesis in the pyrrolidine, piperidine, quinoline, and *iso*quinoline groups, which gives some idea of the breadth of outlook taken in the paper.

The author assumes for the linking of carbon to carbon in the alkaloidal chain only two simple reactions: (1) the aldol condensation, and (2) the similar condensation of the carbinol-amines (containing the group $\cdot\dot{C}(OH)\cdot\dot{N}\cdot$) with substances containing the group $\cdot\dot{C}H\cdot CO\cdot$. For the production of the carbinol-amines he relies on combination of a ketone or aldehyde with ammonia or an amine.

After the alkaloidal skeleton has been built up by these methods, it is necessary to assume further reactions: oxidations, reductions, eliminations of water, or methylation by means of formaldehyde. The work of Collie[28] on the polyketen class is quoted in support of certain steps in the argument, and it is suggested that acetonedicarboxylic acid may be an intermediate compound in the production of acetone by the photochemical decomposition of citric acid in presence of the catalyst uranium oxide.

The following scheme gives an outline of the possible synthesis of tropinone in the plant:

Robinson's Suggested Phytochemical Synthesis of Tropinone.

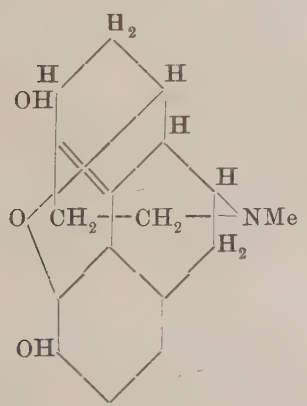


[27] R. Robinson, *T.*, 1917, **111**, 876; *A.*, i, 664.
[28] J. N. Collie, *ibid.*, 1893, **63**, 329; 1907, **91**, 1806.

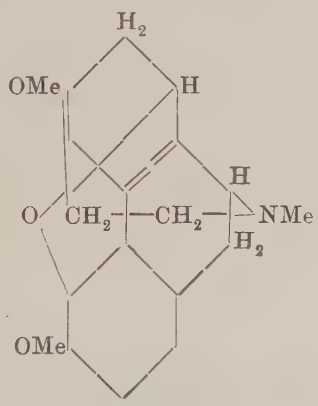
Without exaggeration, it may be said that this paper marks an epoch in the consideration of alkaloid syntheses, and it opens up a new line of thought which may react strongly on the practical methods employed for the commercial production of compounds of this class. Coupled with the same author's synthesis of tropinone, which was dealt with in the preceding section, it suggests that we are on the edge of developments in the study of the alkaloids which were undreamt of at the time last year's Report was published.

The Morphine Alkaloids.

The experimental work in this branch of chemistry has led in recent years to conflicting results in more than one case, and in consequence there has been a good deal of confusion as to the morphine structure. A critical survey[29] of the whole subject has now been published, in which it is sought to harmonise all the experimental data and draw up a formula for morphine itself which will agree with the established facts. As a result of this sifting of the material, the following structures are proposed for morphine and thebaine respectively:



Morphine.

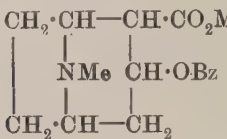


Thebaine.

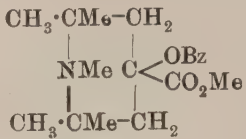
A point of some interest has been raised in connexion with the physiological activity of codeine. It will be recalled that in the case of cocaine substitutes the peculiar physiological activity of the natural substance is paralleled by the behaviour of certain synthetic substances which bear a more or less remote structural resemblance to the true alkaloid's constitution. For example, the

[29] F. Faltis, *Arch. Pharm.*, 1917, **255**, 85; *A.*, i, 411.

following formulæ indicate the kinship in structure between cocaine and eucaine:



Cocaine.



Eucaine.

An attempt has now been made [30] to ascertain whether transpositions of groups in the morphine nucleus leave the physiological character of the compound unaffected; but the results appear to point to the true codeine structure being necessary in order to produce the physiological effect. Thus if the basic properties of the codeine nitrogen atom is destroyed by any means, the alkaloid loses its physiological activity, and does not regain it even when a new amino-group is introduced into the molecule by attachment to the aromatic nucleus of the alkaloid. Hence it is not the mere presence of the amino-group which lends codeine its peculiar character; but, in addition, the amino-group must be active and situated in a particular position in the skeleton. Transposition of the codeine hydroxyl radicle gives analogous results. The new compound has much less physiological activity than codeine. Finally, when a compound is synthesised containing all the characteristic groups of codeine (a methoxylated benzene ring, a nitrogen ring with methylated nitrogen, and an alcohol group), this "pseudo-codeine" shows no resemblance to true codeine in its physiological effects. From this it may be deduced that the root-factor in the physiological activity of both codeine and morphine is to be sought in the position of the nitrogen with regard to the bridged hexamethylene ring.

A new relation has been established between thebaine and codeine by the discovery that when the former is oxidised under certain conditions it yields a hydroxylic ketone, the oxime of which is identical with that derived from bromocodeinone.[31]

Three new methyl derivatives of morphine have been prepared, so that the seven possible ones are all now known.[32]

The Uric Acid Group.

For some time this region of the subject has been almost dormant; but an enormous flood of new material has recently been

[30] J. von Braun and K. Kindler, *Ber.*, 1916, **49**, 2655; *A.*, i, 163.
[31] M. Freund and E. Speyer, *J. pr. Chem.*, 1916, [ii], **94**, 135; *A.*, i, 217.
[32] C. Mannich, *Arch. Pharm.*, 1916, **254**, 349; *A.*, i, 473.

published, which serves to throw a certain amount of light on some minor points. It is quite impossible to summarise the papers, and attention will therefore be directed only to outstanding subjects.

A series of new reactions of uric acid has been described.[33] A method of preparing alloxan, suitable for lecture demonstration, is mentioned.[34] The formula

$$\begin{matrix}\mathrm{NH{-}CO}\\ |\\ \mathrm{CO{\cdot}NH}\end{matrix}\!\!>\!\mathrm{C(OH){\cdot}CO_2H}$$

is suggested for alloxanic acid.[35] Some *spiro*hydantoins have been produced from certain of the uric acid derivatives.[36] A new and simpler method of preparing 9-methyluric acid is described.[37]

One point of interest has been cleared up in the course of this work. It will be remembered that one of the puzzles of the uric acid group was found in the occurrence of three isomeric methyluric acids for which only one formula seemed available, since all of them were supposed to contain a methyl group in the 3-position. These three compounds were designated respectively: α-methyluric acid, δ-methyluric acid, and ζ-methyluric acid. It is stated that δ-methyluric acid is the true 3-methyluric acid, the other two compounds being mixtures containing more or less 9-methyluric acid.[38] Further evidence, however, based on an examination of the crystalline form, absorption spectra, solubility, and acid strength of the three substances leads to the conclusion that the α-acid also is really a molecular compound containing both the 3-methyl- and the 9-methyl-uric acids.[39]

The rest of this series of papers is occupied with an account of derivatives of various uric acids which it is unnecessary to catalogue in detail in this place.[40]

The Ipecacuanha Alkaloids.

During the period covered by this Report a considerable advance has been made in our knowledge of the ipecacuanha alkaloids. In

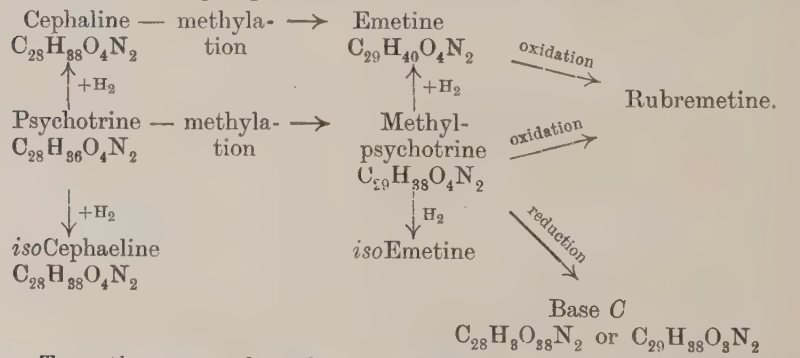
[33] H. Biltz and M. Heyn, *Annalen*, 1916, **413**, 7; *A.*, i., 286.
[34] H. Biltz and M. Heyn, *ibid.*, 60; *A.*, i, 289.
[35] H. Biltz and M. Heyn, *ibid.*, 68; *A.*, i, 289.
[36] H. Biltz, M. Heyn, and M. Bergius, *ibid.*, 77; *A.*, i, 290.
[37] H. Biltz and M. Heyn, *ibid.*, 87; *A.*, i, 291.
[38] H. Biltz and M. Heyn, *ibid.*, 98; *A.*, i, 292.
[39] E. Bülmann and J. Bjerrum, *Ber.*, 1916, **49**, 2515; 1917, **50**, 837; *A.*, i, 177, 588.
[40] H. Biltz, K. Strufe, P. Damm, and M. Heyn, *Annalen*, 1916, **413**, 124; *A.*, i, 293; H. Biltz, M. Bergius, and F. Max, *ibid.*, 1917, **414**, 54; *A.*, i, 589.

1914,[41] three alkaloids from this source had been examined: emetine, cephaeline, and psychotrine, and the relations between them had been established. Psychotrine was found to have the composition $C_{28}H_{36}O_4N_2$. On reduction, it yielded a mixture of cephaeline and *iso*cephaeline, both of which had the composition $C_{28}H_{38}O_4N_2$. Emetine was shown to have the formula $C_{29}H_{40}O_4N_2$ and to be the monomethyl ether of cephaeline. On oxidation, emetine yielded 6 : 7 - dimethoxy*iso*quinoline - 1 - carboxylic acid, thereby establishing the fact that the alkaloids belonged to the *iso*quinoline group.

An extension of this investigation has now been published.[42] A new alkaloid has been isolated, which proves to be the O-methyl ether of psychotrine, and has, in consequence, been named methylpsychotrine. On reduction it yields three bases, namely, emetine, *iso*emetine, and a third substance termed for convenience "Base *C*." Along with methylpsychotrine occurs yet another base, to which the name "emetamine" has been given. Methylpsychotrine and emetine when oxidised produce rubremetine.

Psychotrine and methylpsychotrine contain the imino-group, and it appears probable that the reduction of methylpsychotrine results in the saturation of an ethylenic linking, and not of the linking C:N. The fact that the reduction of psychotrine (or of its methyl ether) results in the formation of two isomeric compounds is ascribed to the creation of a new asymmetric carbon atom in the molecule of the reduction product.

The following table indicates the relations existing between the members of the group and their derivatives:



Two other papers have been published,[43, 44] but they do not throw the same amount of light on the problem.

[41] F. H. Carr and F. L. Pyman, *P.*, 1913, **29**, 226; *T.*, 1914, **105**, 1591.
[42] F. L. Pyman, *T.*, 1917, **111**, 419; *A.*, i, 410.
[43] O. Keller, *Arch. Pharm.*, 1917, **255**, 75; *A.*, i, 409.
[44] P. Karrer, *Ber.*, 1917, **50**, 582; *A.*, i, 409.

Corydalis Alkaloids.

The complications introduced by steric factors are well exemplified in the case of the corydalines.[45] When dehydrocorydaline is reduced, two corydalines are produced. Both are inactive, and it appears that they are probably stereoisomeric, one of them being *r*-corydaline and the other *r*-mesocorydaline. By choosing the experimental conditions properly, either of the two compounds may be obtained alone as the product of the reduction reaction. Separation is effected if necessary by taking advantage of the fact that *r*-mesocorydaline alone crystallises from an ethereal solution of the mixture.

Now when *r*-mesocorydaline is resolved into its optically active components, it is found that the *d*-form is not identical with naturally occurring *d*-corydaline, so that it seemed probable that the natural alkaloid was *d*-corydaline. Attempts to establish this by the resolution of *r*-corydaline into its antipodes failed, so that another method of proof was tried. By the sulphonation of *r*-corydaline it was possible to prepare *r*-corydalinesulphonic acid, and this substance was then resolved by the aid of brucine. The natural *d*-corydaline, in turn, was sulphonated and its optical activity was compared with that of the *d*-antipode of the synthetic sulphonic acid. The identity of the two was thus established, whence it follows that natural and synthetic *d*-corydalines are identical.

Yohimbine and Quebrachine.

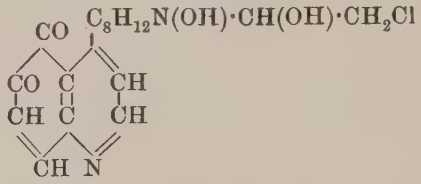
The problem of the identity or non-identity of these two alkaloids has evidently not yet been solved.[46] Although they appear to be easily mistakable for one another in purely chemical tests, it is stated that they are distinguishable in physiological activity,[47] although in their behaviour pharmacologically they have much in common. On this ground, it is suggested that they are not identical, but are members of the same pharmacological group. Attention is directed to the fact that they both, in common with strychnine, give Vitali's reaction.

Other Papers on the Alkaloids.

A number of papers on the cinchona alkaloids have appeared, although none of them can be dealt with in detail here. When a

[45] J. Gadamer and W. Klee, *Arch. Pharm.*, 1916, **254**, 295; *A.*, i, 472.
[46] Compare *Ann. Report*, 1916, 161.
[47] E. Filippi, *Arch. Farm. sperim.*, 1917, **23**, 107; *A.*, i, 582.

quinine salt is treated successively with chlorine and ammonia in solution a green product, thalleioquinine, is obtained. This substance has now [48] been examined, and it is suggested that it is chlorohydroxy-5 : 6-diketocinchonine :



to which one molecule of ammonia is loosely attached. Some degradation reactions in the cinchona group are described, dealing with cincholeupone,[49] *iso*cinchonine,[50] dihydrocinchotoxine,[51] and cinchotine.[52] A new series of "systematic" names for the various alkaloids has been proposed, which may in the end help to make the subject clearer, although at present it merely burdens the reader with a double set of titles to remember. Some substances allied to quinine have been synthesised.[53]

Cyanogen bromide has been employed as a reagent for opening up certain nitrogen ring-compounds, and the new method is of especial interest on account of the fact that the point at which it produces a rupture in the ring is different from that at which the break takes place in the Hofmann reaction of exhaustive methylation. Both hydrohydrastinine and hydrocotarnine have been tested with this reaction, and they are found to give good results; so it appears as if the reaction might be of more general application.[54]

Papers on scopoline bromide,[55] pyraconitine and pyraconine,[56] pelletierine,[57] and methylpelletierine [58] may be referred to by those interested in these subjects.

The Bile Pigments.

It will be recalled that hæmatine, the non-albuminous component of the blood pigment, is the source of bilirubin, a constituent of

[48] A. Christensen, *Ber. Deut. pharm. Ges.*, 1916, **26**, 249; *A.*, i, 51.
[49] P. Rabe, *Ber.*, 1916, **49**, 2753; *A.*, i, 216.
[50] P. Rabe and B. Böttcher, *ibid.*, 1917, **50**, 127; *A.*, i, 281.
[51] A. Kaufmann and P. Haensler, *ibid.*, 702; *A.*, i, 472.
[52] A. Kaufmann, E. Rothlin, and P. Brunnschweiler, *ibid.*, 1916, **49**, 2299; *A.*, i, 50.
[53] P. Rabe, R. Pasternack, and K. Kindler, *ibid.*, 1917, **50**, 144; *A.*, i, 284.
[54] J. von Braun, *ibid.*, 1916, **49**, 2624; *A.*, i, 163.
[55] E. Schmidt, *Arch. Pharm.*, 1917, **255**, 72; *A.*, i, 409.
[56] H. Schulze and A. Liebner, *ibid.*, 1916, **254**, 567; *A.*, i, 470.
[57] K. Hess, *Ber.*, 1917, **50**, 368; *A.*, i, 349.
[58] K. Hess and A. Eichel, *ibid.*, 380; *A.*, i, 350.

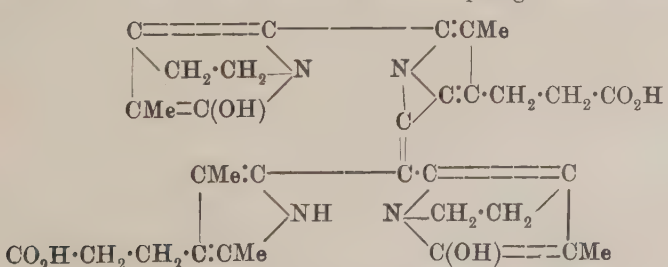
bile. In the present year, the chemistry of bilirubin has advanced a stage, although it must be confessed that the new work renders the problem of the bilirubin constitution even more complicated than before.

Crystalline bilirubin obtained from the gall-stones of the ox has hitherto been constantly associated with some sulphur compound which is difficult to remove; but a recent research [59] has brought to light a method of purification that appears to answer admirably. From the crude bilirubin, a compound, bilirubin-ammonia, is produced by the action of ammonia in dry methyl alcohol, and examination shows that this new derivative is a mixture of two substances, to which the names bilirubin-ammonia-*A* and bilirubin-ammonia-*B* have been given. The *A*-substance is stable, whilst the *B*-modification is unstable. When boiled with chloroform, both substances yield a parent bilirubin, and as these are slightly different in properties they are designated as bilirubin-*A* and bilirubin-*B*. Both of them are free from sulphur, but they contain traces of chlorine derived from the chloroform. Further purification by treatment with methyl alcohol and ammonia and a final boiling with methyl alcohol results in complete purification.

In this way, two bilirubins, known as bilirubin-*AA* and bilirubin-*BB*, are obtained, which appear to be isomeric compounds of the composition $C_{33}H_{36}O_6N_4$.

An investigation of the properties of these two substances shows that the *A*-compound is partly converted into the *B*-modification under the influence of ammonia, whilst the reverse change is favoured by the presence of chloroform. It is suggested that between the *A*- and *B*-compounds there may exist several other (intermediate) bilirubins.

Those who have followed this intricate subject during the last few years and who have watched with increasing scepticism the launching of formula after formula, will perhaps feel but little enthusiasm in their minds for the latest offspring of this class; but



Küster's formula for bilirubin.

[59] W. Küster, *Zeitsch. physiol. Chem.*, 1917, **99**, 86; *A.*, i, 421.

for the sake of historical completeness it may be well to include Küster's recent suggestion in the hope that possibly it may turn out to be a true expression of the structure of this puzzling substance.

The Anthocyanins and other Plant Colouring Matters.

During the period which falls to be dealt with in the present Report, the study of the anthocyanins has been extensive; but the results do not lend themselves to summarisation in a readable form, as they are concerned less with the constitution of typical substances than with an examination of numerous anthocyanins drawn from many different plants. From this wide-ranging investigation,[60] however, it is becoming clear that the almost infinite diversity of colour and tint exhibited by flowers does not imply the existence of an equally diverse series of plant colouring materials. Even from the results which have already been established it seems reasonable to conclude that throughout the flower kingdom only comparatively few basal colouring materials are distributed; and from these simple foundations the infinite variety of floral shades and colours is built up by slight alterations in structure, such as methylation, or by varying the type, number, and mode of attachment of sugar molecules to the chromophoric part of the colouring matter. Pelargonidin, cyanidin, and delphinidin seem to play a preponderant part in the chemistry of plant colouring materials.

Thus the scarlet-red flowers of *Salvia coccinea* and *S. splendens* contain an anthocyanin, salvianin, which has been shown to be a glucoside of pelargonidin, although it differs from any of the hitherto discovered pelargonidin derivatives. The foundation of the colour of the winter aster (*Chrysanthemeum indicum*, L.) is found to be a cyanidin monoglucoside, whilst the colour of the summer aster (*Callistephus Chinensis*) is due to the presence of pelargonidin. The plum, the cherry, and the sloe owe their tints to cyanidin. The pansy is found to contain a delphinidin glucoside, termed violanin. Delphinidin is found also, in the form of derivatives, in petunias. Even the poppy seems to owe its colour to one of the previously known basal compounds.

From this it becomes evident that the study of the plant colouring materials will not be so difficult in the future as it appeared likely to be when the work was begun. Instead of facing an infinite variety of individual pigments, the investigator has, in

[60] R. Willstätter, E. K. Bolton, C. L. Burdick, E. H. Zollinger, and F. J. Weil, *Annalen*, 1916, **412**, 113; *A.*, i, 42.

general, fewer complications to unravel, for at the backbone of the subject it seems probable that there stand only a limited number of chromophoric groups which have been pressed into service and turned to the most varied uses by different plants.

Some other work in the same branch of the subject must be mentioned. An examination has been made[61] of four typical lichens which are used in Ireland for the domestic dyeing of wool in yellowish-brown shades. The most interesting fact which has come to light in this work was found in the case of *Parmelia saxatilis*. This yielded stereocaulic acid and salazinic acid. The latter compound is colourless, yet in spite of this it is the chief dyeing constituent, as it acquires a tint on oxidation.

A synthesis of hydroxyquercetin has been carried out on the lines of Kostanecki's quercetin synthesis.[62]

A. W. Stewart.

[61] H. Ryan and W. M. O'Riordan, *Proc. Roy. Irish Acad.*, 1917, **33**, 91; *A.*, i, 342.

[62] M. Nierenstein, *T.*, 1917, **111**, 4; *A.*, i, 149.

ANALYTICAL CHEMISTRY.

The influence of the war on chemistry in general is reflected in the utilitarian character of many of the recent contributions to analytical chemistry, which have dealt with methods for the examination of industrial by-products or of substances to take the place of those no longer available. This lack of materials has also led to the introduction of methods alternative to those involving the use of reagents, such as glycerol, methyl alcohol, and acetic acid.[1] which are now practically unobtainable, whilst alloys consisting, in the main, of gold and palladium have been used in place of platinum for the manufacture of chemical apparatus.[2]

A large proportion of the analytical papers published during the past year has been of American origin, and there has been a pronounced diminution in the number of European contributions. Some of the latter, published in 1916, were not available in time for the Annual Report of that year, and are therefore mentioned in the present one.

In connexion with analytical apparatus, mention should also be made of a paper dealing with the tests to which porcelain laboratory vessels should be subjected.[3]

Physical Methods.

It was pointed out in last year's Report[4] that the method now in common use of stating the results of viscosity tests in the empirical degrees of particular instruments was unsatisfactory, however carefully those instruments had been standardised, and that to bring the test into line with other physical tests it was advisable that all results should be expressed in terms of absolute viscosity. This is especially necessary in the case of new methods, or of those in which new types of instruments are used, which have

[1] Compare T. Bäck, *Wien. klin. Woch.*, 1917, **30**, 465; *A.*, ii, 520.

[2] See Fahrenwald, *J. Ind. Eng. Chem.*, 1917, **9**, 509. Also *Met. Chem. Eng.*, 1917, **16**, 533.

[3] H. Watkin, *J. Soc. Chem. Ind.*, 1917, **36**, 749.

[4] *Ann. Report*, 1916, 165.

not yet been subjected to variable conditions of working. This necessity has been recognised by the authors of new methods devised during the past year. One of these methods is intended for the examination of minute quantities of oil, such as are frequently separated in analytical work, for which the ordinary standard instruments are quite unsuitable.[5] The apparatus, which is termed a "mercurial viscometer," consists essentially of a capillary tube, in the middle of which is blown a small bulb. The tube has a stop-cock at the base and a receiving cap at the top, and is surrounded by a water-jacket at the required temperature. The tube is filled with mercury, and the oil is introduced into the cap so that it rests on the mercury, and is brought to the definite temperature. The tap is then opened, and the time taken by the mercury in falling from a point above to a point below the capillary bulb is recorded.

The efflux velocity may be converted into Redwood degrees by means of the formula

$$\mathrm{R} = \frac{t}{d}\, k,$$

where t represents the observed time, d the density of the oil at the temperature of the test, and k a constant, which may be obtained by parallel determinations in this and in Redwood's instrument of the efflux velocity of some oil of which larger quantities are available. The absolute viscosity may also be calculated by means of a simple formula, since variations due to the "head" of so small a quantity of oil or to differences in the specific gravity are negligible; but it is essential to accuracy that the dimensions of the capillary bulb tube should be such that the oil does not fall with a sinuous motion.

The standard instruments are also unsuitable for use with very viscous fluids, and the absolute viscosity of such liquids may be more conveniently determined by means of a method based on the measurement of the velocity of the fall of a smooth, rigid sphere, such as a polished steel ball, through the liquid.[6] The absolute viscosity may be calculated by the application of Stokes's law,

$$\frac{K\, 2gR^2(s-s')}{qV},$$

where K represents the coefficients of viscosity, V the observed velocity of fall, g the gravitational constant, s the density of the spherical body, s' that of the liquid, and R the radius of the sphere. Corrections based on data empirically determined must also be

[5] F. M. Lidstone, *J. Soc. Chem. Ind.*, 1917, **36**, 270.

[6] S. E. Sheppard, *J. Ind. Eng. Chem.*, 1917, **9**, 523; *A.*, ii, 359.

applied, since Stokes's law demands that the liquid shall be of infinite extent.

The value of the spectroscopic method of identifying phenols[7] has, in the main, been confirmed, but the method demands the most accurate observation, and it is therefore advisable to make a graph of the absorption bands shown by various solutions of the phenol derivatives.[8]

A physical method[9] affords the most rapid means of accurately estimating the strength of sulphuric acid.[10] The heat of dilution of the acid with water is measured, a vacuum-jacketed tube being used as calorimeter, and the amount of sulphuric acid is calculated by means of the formula

$$x = 100 - 7{\cdot}6\ (3{\cdot}994 - R),$$

which is based on the mean volume of acid delivered by the pipette, the water equivalent of the calorimeter, and the mean results obtained by Pickering.[11]

An interesting application of a physical phenomenon as an indicator in analytical work has been introduced.[12] In titrating lead with ammonium molybdate solution, the colloidal lead molybdate suddenly coagulates when the reaction is complete, and the end-point may be ascertained more sharply in this way than by using tannin as indicator.

Gas Analysis.

There has been further discussion as to the relative merits of different absorbents for oxygen in gas analysis.[13] The use of a solution of sodium pyrogallol[14] is admitted to be cheaper and a specifically more effective absorption agent than potassium pyrogallol, but these advantages are more than counterbalanced by the longer time required for complete absorption of the oxygen.[15] Another reagent recommended as a substitute for alkaline pyrogallol is a 10 per cent. solution of hyposulphite of zinc or sodium.[16]

For the estimation of ozone in air, a method has been based on the fact that a solution of ammonium ferrous sulphate is

[7] H. Gsell, *Zeitsch. anal. Chem.*, 1916, **55**, 417; *A.*, 1916, ii, 584.

[8] J. Formánek and J. Knop, *ibid.*, 1917, **56**, 273; *A.*, ii, 503.

[9] H. D. Richmond and J. E. Merreywether, *Analyst*, 1917, **42**, 273; *A.*, ii, 503.

[10] Compare H. Howard, *J. Soc. Chem. Ind.*, 1910, **29**, 3.

[11] *T.*, 1890, **57**, 64.

[12] J. F. Sacher, *Kolloid-Zeitsch.*, 1916, **19**, 276; *A.*, ii, 180.

[13] See *Ann. Report*, 1916, 168.

[14] J. W. Shipley, *J. Amer. Chem. Soc.*, 1916, **38**, 1687; *A.*, 1916, ii, 571.

[15] R P. Anderson, *J. Ind. Eng. Chem.*, 1916, **8**, 999; *A.*, ii, 39.

[16] L. Descamps, *Bull. Assoc. chim. Sucr. Dist.*, 1916, **34**, 34; *A.*, ii, 216.

immediately oxidised by ozone, but not by air free from ozone, and on the titration of the unoxidised iron salt by means of standard permanganate solution.[17]

The objection to this method is that it is not specific for ozone, the ferrous salt being oxidised as readily by hydrogen peroxide as by ozone. Similar criticism may be brought against other methods, such as those in which the ozone is oxidised by potassium permanganate,[18] or in which potassium iodide or bromide is used as the reagent.[19] The most trustworthy method of estimating atmospheric ozone in the presence of nitrogen oxides and hydrogen peroxide is by the use of a slightly alkaline solution of sodium nitrite.[20] This is oxidised to nitrate by ozone, whilst nitrogen peroxide yields nitrate and nitrite, and hydrogen peroxide is not affected. In making an estimation, two samples of the air are taken, one of which is passed through a tube containing chromic acid and manganese dioxide, and the other through a tube containing chromic acid only. The nitrite solution is then introduced into the two bottles, and the amount of nitrite subsequently estimated colorimetrically. The first bottle will contain only nitrogen peroxide, and the increase in the quantity of nitrite will afford a measure thereof; in the second bottle, both ozone and nitrogen peroxide will be present, and the difference between the two estimations will be equivalent to the ozone present.

The method of estimating gasoline vapour in air by combustion and condensation with liquid air[21] has been found to be untrustworthy, the combustion being incomplete when more than 5 or 6 per cent. of gasoline is present.[22]

Since colorimetric methods, when trustworthy,[23] have the advantages of speed and sensitiveness, a colorimetric method of estimating carbon dioxide in the air appears likely to prove a useful addition to tests which have often to be employed at a distance from the laboratory.[24] The principle of the process is that when a solution of sodium hydrogen carbonate becomes saturated with the carbon dioxide present in a current of air, the reaction of the liquid will afford a measure of the relative amounts of carbon dioxide and sodium hydrogen carbonate, whilst

[17] David, *Compt. rend.*, 1917, **164**, 430; *A.*, ii, 216.
[18] E. H. Keiser and L. McMaster, *Amer. Chem. J.*, 1908, **39**, 96.
[19] Compare W. Hayhurst and J. N. Pring, *T.*, 1910, **97**, 868.
[20] F. L. Usher and B. S. Rao, *ibid.*, 1917, **111**, 799; *A.*, ii, 502.
[21] G. A. Burrell and I. W. Robertson, *J. Ind. Eng. Chem.*, 1915, **7**, 112; *A.*, 1915, ii, 184.
[22] R. P. Anderson, *ibid.*, 1917, **9**, 142; *A.*, ii, 338,
[23] Compare W. M. Dehn, *J. Amer. Chem. Soc.*, 1917, **39**, 1392; *A.*, ii, 499.
[24] H. L. Higgins and W. M. Marriott, *ibid.*, 68; *A.*, ii, 270.

the proportion of carbon dioxide absorbed is a function of its partial pressure in the particular air and is not affected by the volume of air which passes through the liquid after the latter has been saturated with carbon dioxide.

In applying the test, the air is passed through a standard solution of sodium hydrogen carbonate containing a suitable indicator, such as phenolsulphonephthalein,[25] until no further change of colour appears, and the colour is then compared with those of standard solutions of potassium hydrogen phosphate and disodium hydrogen phosphate prepared to correspond with air containing known quantities of carbon dioxide.

A method of estimating gases of the argon group has been based on the fact that, unlike nitrogen and other gases, they are not absorbed by metallic calcium heated to dull redness (450° to 550°).[26] Argon may thus be directly separated from air, but in the case of gaseous mixtures, a preliminary separation of such gases as carbon monoxide, carbon dioxide, and methane is advisable.

Agricultural Analysis.

There have been few additions during the past year to analytical processes as applied to agriculture, although several well-known methods have been studied and modifications of them devised with a view to obviate possible errors.

For example, in the estimation of nitrates in soil by the phenoldisulphonic acid method,[27] it has been found that the colour of the reaction mixture is affected by light, and that the comparison must therefore be made as rapidly as possible. The loss of nitrates caused by the presence of chlorides and sulphates may be prevented by adding a small excess of calcium hydroxide before the evaporation and flooding the residue with a large excess of the reagent. By the use of this modification, no loss of nitrates need be feared if potassium alum, which is the most efficient flocculating agent, be used for treating the soil solution.[28]

Ammonia may be accurately estimated by slowly distilling a mixture of the soil with magnesium oxide and water under diminished pressure, and finally passing a current of ammonia-free air through the flask. The distillate is collected in standard

[25] Compare H. A. Lubs and S. F. Acree, *J. Amer. Chem. Soc.*, 1916, **38**, 2772; *A.*, ii, 97.

[26] A. Sieverts and R. Brandt, *Zeitsch. angew. Chem.*, 1916, **29**, 402; *A.*, ii, 103.

[27] C. W. Davis, *J. Ind. Eng. Chem.*, 1917, **9**, 290; *A.*, ii, 329.

[28] See *Water Analysis*, p. 169.

sulphuric acid, which is subsequently titrated with standard alkali, Congo-red being used as indicator. In addition to ammonia, volatile amines and bases will also distil, but the ammonia may be separated by precipitation as ammonium magnesium phosphate and distillation of the precipitate with sodium hydroxide. It has been found, however, that the amounts of amines and volatile bases distilling with the ammonia, either from soils or liquid manures, are practically negligible.[29]

In the estimation of nitrogen in soils by the Gunning method, the addition of a small amount of copper wire during the digestion causes the subsequent distillation to proceed more regularly, whilst the results will then agree closely with those obtained by Kjeldahl's method.[30]

The method of estimating organic carbon by combustion with copper oxide frequently gives higher results than the wet method, in which potassium dichromate and sulphuric acid are used for the combustion. This does not necessarily prove that the former method is the more accurate, for it has been found that in the case of soils which contain calcite included within quartz grains, the combustion with copper oxide causes liberation of carbon dioxide from the calcite.[31]

A convenient apparatus has been devised for the rapid estimation of carbon dioxide from the carbonates in soil. The flask in which the soil is treated with hydrochloric acid is connected with a mercury manometer, and the pressure of the gas acts on a float, the movements of which are mechanically recorded. The rate of evolution of the carbon dioxide thus affords an index of the nature of the carbonates in the soil.[32]

Further attention has been given to the question of the solubility of phosphates in acids.[33] It has been found that certain organic acids dissolve more phosphoric acid from superphosphates than from mineral phosphates. The high solubility of phosphoric acid in citric acid solutions is due to the formation of a complex citrophosphate in combination with aluminium and ferric iron, and it is probable that similar complex compounds are formed in the case of other organic acids, such as formic and acetic acids.[34]

Both tricalcium and dicalcium phosphates are soluble in 2 per

[29] W. I. Baragiola and O. Schuppli, *Landw. Versuchs-Stat.*, 1917, **90**, 123; *A.*, ii, 380.

[30] W. L. Latshaw, *J. Ind. Eng. Chem.*, 1916, **8**, 1127; *A.*, ii, 100.

[31] E. C. Shorey and W. H. Fry, *ibid.*, 1917, **9**, 588; *A.*, ii, 422.

[32] G. Hutin, *Ann. Chim. anal.*, 1917, **22**, 158; *A.*, ii, 541.

[33] See *Ann. Report*, 1916, 170.

[34] A. Aita, *Ann. Chim. Applicata*, 1917, **9**, 200.

cent. citric acid solution, and hence this reagent cannot be used to differentiate between the two phosphates, as commonly accepted. This affords a further reason against the use of the citric acid method of estimating phosphoric acid.[35]

The Pemberton method of estimating phosphoric acid by precipitation as phosphomolybdate gives trustworthy results provided that the precipitation is made with not too old a reagent and between 30° and 40°. In applying the method to acid phosphates, it is advisable to make a parallel estimation on a standard phosphate rock, adding the same amount of sulphuric acid, after solution in nitric acid, as was used in the case of the sample.[36]

Organic Analysis.

Qualitative.—The principal addition, during the past year, to the methods of identifying organic compounds has been based on the properties of the various crystalline derivatives formed by the interaction of *p*-nitrobenzyl bromide and alkali salts of organic acids. These esters have definite melting points and differ in their solubility in alcohol, and so may be used for distinguishing between the different acids in a mixture.[37] By this means, it has been found possible to identify benzoic acid in presence of acetic, tartaric, citric, salicylic, and *p*-toluenesulphonic acids, but the method is less suitable for the identification of aliphatic acids, many of which yield oily instead of crystalline derivatives.[38] In some cases, the use of *p*-nitrobenzyl chloride or iodide is preferable, the iodide, for instance, yielding with dibasic acids very insoluble esters, from which the unaltered iodide can readily be separated.[39]

A modification of the method may be used for the identification of alcohols. The alcohol is heated with phthalic anhydride, and the sodium salt of the resulting acid ester is converted by means of *p*-nitrobenzyl bromide into the corresponding mixed phthalic ester, which in many cases has a distinctive melting point.[40]

Phenols also may be identified in a similar manner by the characteristics of the ethers obtained by the interaction of the potassium or sodium phenoxide and *p*-nitrobenzyl bromide.[41]

A new method of identifying the fatty acids in a fat is based on the hydrolysis of glycerides by heating them in a sealed tube

[35] A. A. Ramsay, *J. Agric. Sci.*, 1917, **8**, 277; *A.*, ii, 413.
[36] P. M. Shuey, *J. Ind. Eng. Chem.*, 1917, **9**, 367; *A.*, ii, 269.
[37] E. E. Reid, *J. Amer. Chem. Soc.*, 1917, **39**, 24; *A.*, i, 333.
[38] E. Lyons and E. E. Reid, *ibid.*, 1727; *A.*, i, 559.
[39] J. A. Lyman and E. E. Reid, *ibid.*, 701; *A.*, i, 334.
[40] E. E. Reid, *ibid.*, 1249; *A.*, i, 455.
[41] E. E. Reid, *ibid.*, 304; *A.*, i, 333.

with an aromatic amine, such as aniline or α-naphthylamine, the resulting amides having distinctive melting and boiling points under diminished pressure. The decomposition is not quantitative, but is approximately proportional to the amounts of fatty acids present.[42]

Another new group-reaction has been based on the formation of azomethines by the condensation of aromatic aldehydes with sulphonated aromatic amino-compounds. Many of these azomethines have characteristic colours, which may be used for the identification of the aldehydes.[43]

A general method for the detection of aldehydes, ketones, and phenols in essential oils depends on the fact that these compounds, unlike alcohols and hydrocarbons, give distinctive colorations with sodium arsenotungstate or arsenotungstomolybdate.[44]

Turning to the reactions of individual substances, it will be found that a few new tests have been devised, and the sensitiveness of some of the older tests has been ascertained. For the detection of hydrocyanic acid,[45] the guaiacol, or Schönbein-Pagenstecher's method, is the most sensitive reaction, being capable of detecting 0·00001 per cent. of cyanogen, but it is not specific, and for general purposes the Prussian blue test is the most trustworthy, although under certain conditions the thiocyanate test may be useful. The picric acid test is less sensitive than any of these tests, and has also the drawback that similar colorations are obtained with reducing substances, such as sugar and sulphur dioxide.[46]

Both citric and malonic acids are oxidised by an acetic acid solution of potassium permanganate to acetone, which may be identified by the iodoform test. Citric acid may then be distinguished from malonic acid by yielding a crystalline barium citrate.[47]

A solution of titanic acid in sulphuric acid affords a means of distinguishing between the two naphthols, α-naphthol giving a bright green and β-naphthol a blood-red coloration.[48]

Resorcinol may be detected by the green coloration which it gives with a solution of cobalt chloride followed by concentrated ammonia and alcohol. Under similar conditions, catechol and

[42] E. de'Conno, *Gazzetta*, 1917, **47**, i, 93; *A.*, i, 386.
[43] P. Pooth, *Schweiz. Apoth. Zeit.*, 1916, **54**, 377; *A.*, ii, 52.
[44] L. Guglialmelli, *Anal. Soc. Quim. Argentina*, 1917, **5**, 11; *A.*, ii, 514.
[45] See *Ann. Report*, 1916, 173.
[46] G. W. Anderson, *J. Soc. Chem. Ind.*, 1917, **36**, 195; *A.*, ii, 183.
[47] T. C. N. Broeksmit, *Pharm. Weekblad*, 1917, **54**, 686; *A.*, ii, 429.
[48] G. Denigès, *Ann. Chim. anal.*, 1916, **21**, 343; *A.*, ii, 48.

pyrogallol give a brown coloration, whilst a solution of phenol remains colourless.[49]

A new reaction for *d*-galactose has been described. This sugar, when heated with *o*-tolylhydrazine, yields an *o*-tolylhydrazone (m. p. 176°), whereas no corresponding hydrazone is formed by arabinose, xylose, rhamnose, dextrose, mannose, or lævulose.[50]

Quantitative.—As the micro-balance required for Pregl's method of micro-combustion[51] is now unobtainable, a modification of the method has been devised, in which larger quantities of material (11 to 22 milligrams) are weighed with an ordinary balance. The packing of the combustion tube has also been modified, whilst soda-lime in a tube with a ground-in joint replaces the potash absorption bulb. A "blank" estimation should be made under parallel conditions to obtain the correction for the hydrogen results, which are sometimes 0·1 to 0·15 per cent. too high. With this correction, the results agree well with those obtained by the ordinary methods of combustion.[52]

For the rapid estimation of halogens in organic compounds, the substance is fused with a mixture of sodium peroxide, potassium nitrate, and powdered benzoic acid or sucrose (to ensure uniform fusion). The oxidised mixture is treated with excess of silver nitrate prior to acidification with nitric acid, and the excess of silver titrated. Hydrazine sulphate is added to the hot solution containing the precipitated haloid to reduce any halogen oxy-acids which may have been formed.[53]

A trustworthy method of estimating silver in organic compounds has been based on the interaction of alkali cyanides and silver salts, and precipitation of the silver in the metallic form or as sulphide from the argenticyanide solution.[54]

In the ordinary method of estimating mercury in organic compounds by combustion with quicklime, the distilled mercury is frequently contaminated with tarry matter. This may be obviated by mixing the mercury compound with dry calcium sulphate and excess of quicklime, and distilling the mercury in the usual way.[55]

In estimating ethyl alcohol by Dupré's method,[56] the preliminary

[49] F. C. Krauskopf and G. Ritter, *J. Amer. Chem. Soc.*, 1916, **38**, 2182; *A.*, ii, 48.

[50] A. W. van der Haar, *Rec. trav. chim.*, 1917, **37**, 108; *A.*, ii, 515.

[51] E. Abderhalden, "Handbuch der Biochem. Arbeitsmethoden," [ii], **5**, 1307.

[52] L. E. Wise, *J. Amer. Chem. Soc.*, 1917, **39**, 2055; *A.*, ii, 541.

[53] J. F. Lemp and H. G. Broderson, *ibid.*, 2069; *A.*, ii, 539.

[54] H. J. Lucas and A. R. Kemp, *ibid.*, 2074; *A.*, ii, 542.

[55] J. E. Marsh and O. G. Lye, *Analyst*, 1917, **42**, 84; *A.*, ii, 219.

[56] A. Dupré, *Journ. Chem. Soc.*, 1867, **20**, 495.

separation of the alcohol is often not quantitative. Better results may be obtained by removing the alcohol by means of a current of air, absorbing it in concentrated sulphuric acid, oxidising the mixture with potassium dichromate solution, and distilling the acetic acid. Acetaldehyde and ethyl acetate also yield acetic acid on oxidation, whilst methyl alcohol is oxidised to carbon dioxide and water, but acetone is only slightly oxidised.[57]

The most satisfactory means of estimating water in alcohol is to determine the specific gravity of the liquid before and after dehydration with potassium carbonate.[58] The percentage of alcohol may then be obtained by reference to a curve.[59]

A new method of estimating butyric acid mixtures containing also formic acid and acetic acid depends on the solubility of quinine butyrate and the insolubility of quinine formate and acetate in carbon tetrachloride. Quinine butyrate may be identified by its melting point, 77·5°.[60]

A large amount of experimental work has been done in connexion with Duclaux's method of estimating volatile fatty acids by distillation in a current of steam,[61] and various applications of the method have been tested. Experiments with mixtures of pure propionic, butyric, valeric, and hexoic acids have shown that the values obtained under the specific conditions previously determined[62] may be regarded as trustworthy. When only two acids are present, the amount of each may be obtained from the results of the distillation, and the ratio between them calculated for each fraction. In the absence of other acids, there should be a fairly close agreement between the ratios, and the mean ratio will give an indication of the molecular proportion.[63] By a slight modification, the method may be used for the estimation of butyric acid in acetic anhydride and for testing the purity of substituted malonic acids.[64]

In one modification of the method, the volume of the aqueous solution is kept at a constant volume of 150 c.c. Under such conditions, the results, when plotted on a logarithmic chart, form a straight line in the case of a single acid, but a curve when a mix-

[57] A. W. Dox and A. R. Lamb, *J. Amer. Chem. Soc.*, 1916, **38**, 2561; *A.*, ii, 47.

[58] Compare E. Mallinkrodt and A. D. Alt, *J. Ind. Eng. Chem.*, 1916, **8**, 807; *A.*, 1916, ii, 583.

[59] R. L. Perkins, *ibid.*, 1917, **9**, 52; *A.*, ii, 393.

[60] J. K. Phelps and H. E. Palmer, *J. Biol. Chem.*, 1917, **29**, 199; *A.*, ii, 278.

[61] E. Duclaux, *Ann. Inst. Pasteur*, 1895, **9**, 265; *A.*, 1896, ii, 504.

[62] H. D. Richmond, *Analyst*, 1908, **33**, 305; *A.*, 1908, ii, 495, 754.

[63] H. D. Richmond, *ibid.*, 1917, **42**, 125; *A.*, i, 316.

[64] H. D. Richmond, *ibid.*, 133; *A.*, ii, 277.

ture of acids is present, and the probable composition and approximate proportion of these acids may be found by reference to the chart.[65]

The method has been subjected to criticism on the ground that by the use of Duclaux's constants, practically identical results may be calculated for mixtures of totally different proportions of acids;[66] but in reply to this criticism, experiments have been cited to show that the figures are quite trustworthy when based on results obtained with pure acids, although not more than three acids can be satisfactorily estimated in the same fraction.[67] If four or more acids are present, it is essential to separate the liquid into fractions containing three acids. The main essential is that the distillation should always be made in a uniform manner.[68]

It is a general, although incorrect assumption, that in estimating phenol in tar acids, the fraction distilling up to about 200° contains the whole of the phenol.[69] It is possible, however, by the addition of a suitable proportion of *o*-cresol to prepare a mixture which will yield the whole of its phenol in the first fractions of the distillate.[70] By determining the crystallisation points of successive fractions distilled from a tar oil and reference to a table, the proportion of phenol may be estimated with sufficient accuracy for commercial purposes.[71] For more accurate work, however, it is necessary to distil the purified sample under standard conditions and to redistil the united lower fractions, so as to obtain a final fraction distilling up to 197°. From the specific gravity and crystallisation point of this fraction, the percentage of phenol may be obtained by reference to standard curves.[72]

A colorimetric method of estimating minute quantities of aniline has been based on a comparison of the coloration given by the solution on treatment with standard solutions of calcium hypochlorite and sodium hydroxide with the colorations obtained under the same conditions with standards containing up to 0·07 milligram of aniline. The method is accurate within about 0·003 milligram.[73]

[65] D. C. Dyer, *J. Biol. Chem.*, 1917, **28**, 445; *A.*, ii, 157.

[66] F. W. Upson, H. M. Plum, and J. E. Schott, *J. Amer. Chem. Soc.*, 1917, **39**, 731; *A.*, ii, 277.

[67] A. R. Lamb, *ibid.*, 746; *A.*, ii, 277.

[68] L. J. Gillespie and E. H. Walters, *ibid.*, 2027; *A.*, ii, 549.

[69] Compare R. Masse and H. Leroux, *Compt. rend.*, 1916, **163**, 361; *A.*, 1916, ii, 650.

[70] J. J. Fox and M. F. Barker, *J. Soc. Chem. Ind.*, 1917, **36**, 842; *A.*, ii, 513.

[71] R. Masse and H. Leroux, *Bull. Soc. chim.*, 1917, [iv], **21**, 2.

[72] J. M. Weiss and C. R. Downs, *J. Ind. Eng. Chem.*, 1917, **9**, 569; *A.*, ii, 428.

[73] E. Elvove, *ibid.*, 953; *A.*, ii, 584.

The method of estimating nitrotoluenes by reduction with stannous chloride, followed by the addition of alkaline tartrate and titration with iodine, is not altogether trustworthy, especially when alcohol has to be used to dissolve the compound. Better results may be obtained by omitting the treatment with alkaline tartrate and titrating the excess of stannous chloride with an acid solution of iodine. The results are usually about 96 per cent. below the theoretical amounts.[74]

A few new methods of analysing fats have been introduced. Glycerides may be fractionally separated by dissolving the fat in two or more solvents, such as alcohol and ether, one of which is more volatile and has a greater solvent action than the other. Then, by aspirating air through the solution, gradual evaporation accompanied by a considerable reduction of temperature takes place, and the glycerides may be successively removed as they separate in the order of their insolubility. Similar fractions are combined and subjected to further fractionation. By this means, the mixed glycerides, oleodistearin and dioleopalmitin, have been isolated from tallow. The method is also applicable to the detection of beef and mutton fat in butter fat, the latter yielding a very much smaller amount of insoluble glycerides than butter fat containing 20 per cent. of tallow.[75]

The calorimetric method of measuring the thermal values of oils[76] has been extended to the determination of the Maumené value, and it has been shown that the values thus obtained under standard conditions with typical oils stand in close relationship to the iodine values.[77]

An analytical method based on catalytic hydrogenation has been devised for the detection of rape oil in olive oil. An ethereal solution of the more unsaturated fatty acids, separated by the lead–ether method, is hydrogenated in the presence of finely divided palladium, and the resulting product is fractionally crystallised from alcohol. In the presence of rape oil, behenic acid, formed by the hydrogenation of the original erucic acid, will be obtained, and may be identified by its melting point and sparing solubility in alcohol.[78]

The oxidisability value of oils[79] affords a means of determining

[74] E. de W. S. Colver and E. B. R. Prideaux, *J. Soc. Chem. Ind.*, 1917, **36**, 480; *A.*, ii, 512.

[75] A. Seidenberg, *J. Ind. Eng. Chem.*, 1917, **9**, 855; *A.*, i, 626.

[76] See *Ann. Report*, 1916, 180.

[77] J. W. Marden and (Miss) M. V. Dover, *J. Ind. Eng. Chem.*, 1917, **9**, 858.

[78] R. Biazzo and S. Vigdorcik, *Ann. Chim. Applicata*, 1916, **6**, 185.

[79] See *Ann. Report*, 1916, 180.

the suitability of oils and fats for medicinal purposes. In the case of fresh fats, this value should not exceed 10, but castor oil, even when old and having a high acid value, contains only small amounts of volatile aldehydic and ketonic compounds, and therefore shows low oxidisability values.[80]

Reference may also be made to a simplified volumetric method of analysing sulphonated oils, the results obtained being in close agreement with those given by the usual gravimetric method.[81]

For the estimation of sucrose, dextrose, lævulose, and maltose in admixture, methods based solely on the cupric reducing power may give erroneous results, owing to cupric oxide dissolving in the hot alkaline solution.[82] In such cases, the method of oxidising the sugars by means of bromine[83] is more trustworthy. Bromine oxidises dextrose and maltose quantitatively at the normal temperature, whilst lævulose is only oxidised to a limited extent. When dextrose is the only other sugar present, lævulose may be directly estimated by the bromine oxidation method. The results thus obtained in the analysis of honey and jam are sufficiently trustworthy for commercial purposes, although the method is less accurate than the more tedious method of enzymic hydrolysis.[84] In other cases, the method may be conveniently used in conjunction with determinations of the cupric reducing power and optical rotation.

A sensitive method of detecting and estimating lævulose in the presence of dextrose has been based on boiling lævulose with a 0·2 per cent. solution of orcein and 85 per cent. phosphoric acid, a yellow coloration being produced. This is matched with the colorations obtained under the same conditions with standard solutions of lævulose. When applied qualitatively, the test is capable of detecting lævulose in 1 c.c. of a 0·08 per cent. solution.[85]

Free and combined galactose may be estimated by a modification of Creydt's method,[86] in which the solution is oxidised with nitric acid and the resulting mucic acid separated and weighed. Tables showing the corresponding quantities of galactose have been constructed.[87]

For the estimation of aldose sugars, a new method has been

[80] G. Issoglio, *Ann. Chim. Applicata*, 1917, **7**, 187.
[81] R. Hart, *J. Ind. Eng. Chem.*, 1917, **9**, 850.
[82] (Miss) E. G. Wilson and W. R. G. Atkins, *Biochem. J.*, 1916, **10**, 504; *A.*, 1916, ii, 652.
[83] E. C. Kendall, *Analyst*, 1912, **37**, 205; *A.*, 1912, ii, 393.
[84] W. R. G. Atkins, *ibid.*, 1917, **42**, 12; *A.*, ii, 157.
[85] L. Loewe, *Proc. Soc. Exp. Biol., Med.* 1917, **12**, 71; *A.*, ii, 49.
[86] Creydt, *Diss.*, Erlangen, 1888.
[87] A. W. van der Haar, *Chem. Weekblad*, 1916, **13**, 1204.

based on their quantitative oxidation by means of a solution of iodine in sodium carbonate solution, the excess being afterwards titrated with thiosulphate. The method has the drawback that other substances besides aldose sugars will reduce hypoiodite solution.[88]

In estimating sugars in the presence of gum arabic, the latter may be more completely precipitated by a mixture of alcohol with basic lead acetate than by basic lead acetate alone, but, even then, the presence of gum in the filtrate interferes with the polarimetric estimation of invert-sugar.[89]

In a method of estimating glutose, the non-fermentable sugar in cane molasses, the pentoses are first destroyed by fermenting the dilute acidified solution for three days with a bottom-fermentation yeast, and determining the reducing power of the clarified fermented liquid. For this purpose, the reducing power of glutose is taken as half that of invert-sugar.[90]

For the polarimetric estimation of starch in the presence of other optically active substances, advantage has been taken of the fact that lead tannate will precipitate starch, even after gelatinisation by heat. The amount of starch may be calculated from the results of the polarisation before and after the precipitation.[91] A new method for the direct estimation of starch has also been described, in which the starch is dissolved in calcium chloride solution and precipitated with iodine, the starch-iodide being then decomposed with alcohol and the starch weighed.[92]

Several modifications of the methods of estimating alkaloids have been published. The inaccuracies of the ordinary methods of estimating theobromine are obviated by precipitating the alkaloid as the silver compound, estimating the nitrogen in the precipitate by Kjeldahl's method, and calculating the amount of theobromine from the result. The presence of even considerable quantities of caffeine does not interfere with the estimation.[93]

A trustworthy method of estimating morphine has been based on its quantitative oxidation in a dilute sulphuric acid solution by means of iodic acid, two molecules of the alkaloid absorbing three atoms of oxygen. Other alkaloids, including codeine and narcotine,

[88] J. Bougault, *Compt. rend.*, 1917, **164**, 1008; *A.*, ii, 395.
[89] G. Savini, *Ann. Chim. Applicata*, 1916, **6**, 250.
[90] H. Pellet, *Ann. Chim. anal*, 1917, **22**, 43; *A.*, ii, 223.
[91] C. Baumann and J. Grossfeld, *Zeitsch. Nahr. Genussm.*, 1917, **33**, 97; *A.*, ii, 223.
[92] T. von Fellenberg, *Mitt. Lebensmittelunters. Hyg.*, 1916, **7**, 369; *A.*, ii, 342.
[93] Mrs. N. Radford and G. Brewer, *Analyst*, 1917, **42**, 274; *A.*, ii, 519.

also absorb oxygen, so that the method is unsuitable for the estimation of morphine in opium.[94]

Attention has been directed to the possibility of errors in the colorimetric method of estimating creatine and creatinine, owing to the presence of impurities in the picric acid. Much of the commercial picric acid now sold gives colorations with sodium hydroxide, and is quite unsuitable for the purpose of this estimation.[95]

Inorganic Analysis.

Qualitative.—A modification of Penfield's test for water may be used for the detection of carbon in minerals and other substances. The finely divided substance is mixed with lead chromate, which must be free from carbon, and the mixture is heated in a horizontal, narrow glass tube, one end of which is closed, whilst near the open end there is a bulb containing a clear solution of barium hydroxide. In the presence of as little as 0·003 milligram of carbon, a white film will be produced on the surface of the reagent.[96] Another delicate test for carbon is to heat the substance with a large excess of potassium azide, which in the presence of carbon will produce potassium cyanide, easily recognisable by the Prussian-blue test. The reaction is rendered more sensitive by adding metallic potassium to the mixture.[97]

The method of detecting phosphorus by the reduction of its compounds to phosphorus hydride by means of zinc and hydrochloric acid is slow, but under the best conditions is capable of detecting 0·0025 gram of phosphorus in the form of hypophosphite. The reduction should be effected at about 55°, the gas absorbed by means of silver nitrate solution, and the precipitate again reduced. The coloration of the phosphorus flame may be recognised as distinctly by the unaided eye as by the use of the spectroscope.[98]

Traces of manganese may be detected even in the presence of other metals by the rose-red coloration which they give when treated in slightly alkaline solution with an alkali oxalate, followed by acetic acid.[99]

The value of the hydrogen peroxide test for copper[1] has been

[94] J. N. Rakshit, *J. Soc. Chem. Ind.*, 1917, **36**, 989 ; *A.*, ii, 553.
[95] O. Folin and E. A. Doisy, *J. Biol. Chem.*, 1917, **28**, 349 ; *A.*, ii, 159.
[96] W. G. Mixter and F. L. Haigh, *J. Amer. Chem. Soc.*, 1917, **39**, 374 ; *A.*, ii, 267.
[97] E. Müller, *J. pr. Chem.*, 1917, [ii], **95**, 53 ; *A.*, ii, 269.
[98] H. J. Lemkes, *J. Pharm. Chim.*, 1917, **15**, 177.
[99] V. Macri, *Boll. chim. farm.*, 1917, **56**, 377 ; *A.*, ii, 511.
[1] Compare J. Sperber, *Schweiz. Apoth. Zeit*, 1915, **53**, 717 ; *A.*, 1916, ii, 314.

confirmed, and it has been found that the sensitiveness of the reaction is increased by the addition of sodium hydrogen carbonate.[2] The violet coloration produced when hydrogen peroxide is treated with tartaric acid and a ferrous salt and then with an alkali hydroxide, is due to the formation of a ferric compound of hydroxytartaric acid. It is not a trustworthy reaction for tartaric acid, but under certain conditions may be used as a sensitive test for hydrogen peroxide.[3]

A delicate test for gallium has been based on the insolubility of gallium ferrocyanide in dilute hydrochloric acid and the relative solubility of the metals which are usually separated with gallium. For the separation of gallium from aluminium, before applying this test, the mixed chlorides may be treated with ether, in which gallium chloride is soluble.[4]

For the detection of germanium and its separation from arsenic, the zinc oxide or other substance under examination is distilled with concentrated hydrochloric acid, to which potassium permanganate[5] has been added to prevent reduction of arsenic sulphide and distillation of arsenic. In the presence of 0·0001 gram of germanium, the distillate will give a white precipitate with hydrogen sulphide.[6]

The difference between the respective solubilities of the fluorides of calcium, barium, and strontium affords a rapid and fairly delicate means of detecting calcium in the presence of the other metals. On adding a solution of barium fluoride to 10 c.c. of a solution containing as little as 0·003 gram of calcium chloride, a distinct turbidity is at once produced, even in the presence of seven times the quantity of strontium chloride and one hundred times the quantity of barium chloride.[7]

In using palladium chloride as a test for iodides, it is necessary to take into account the fact that thiocyanates, ferrocyanides, and ferricyanides interfere with the reaction. The addition of an excess of the reagent and boiling the liquid tend to check the interference.[8]

[2] F. Mayer and W. H. Schramm, *Zeitsch. anal. Chem.*, 1917, **56**, 129; *A.*, ii, 334.

[3] F. Mayer and W. H. Schramm, *loc. cit.*

[4] P. E. Browning and L. E. Porter, *Amer. J. Sci.*, 1917, [iv], **44**, 221; *A.*, ii, 544.

[5] Compare G. H. Buchanan, *J. Ind. Eng. Chem.*, 1916, **8**, 585; *A.*, 1916, ii, 486.

[6] P. E. Browning and S. E. Scott, *Amer. J. Sci.*, 1917, [iv], **44**, 313; *A.*, ii, 546.

[7] Z. Karaoglanow, *Zeitsch. anal. Chem.*, 1917, **56**, 138; *A.*, ii, 333.

[8] L. J. Curtman and B. R. Harris, *J. Amer. Chem. Soc.*, 1917, **39**, 266; *A.*, ii, 267.

Many alkaloids form insoluble perchlorates, and so may be used for the detection of the perchloric ion. For example, strychnine, brucine, and morphine yield perchlorates which may be recognised under the microscope by their crystalline form. Of the three alkaloids, strychnine sulphate is the most sensitive reagent, being capable of detecting the perchloric ion in a 0·1 per cent. solution.[9]

Quantitative.—Among other criticisms against the use of potassium dichromate as a standard for volumetric methods,[10] it has been asserted that liberation of iodine may occur in the course of the oxidation of the potassium iodide solution, probably owing to the formation of an intermediate iodochromate, $ICrO_3K$. Such a source of error, if unavoidable, would render the method untrustworthy, but experiments have shown that, in the case of dilute solutions, at all events, there is no risk of the formation of this compound.[11]

Oxalic acid, when purified by recrystallisation, is one of the most suitable standards for alkalimetry.[12] The most accurate method of using it is to titrate its solution with alkali until the neutralisation point is nearly reached, then to add sufficient calcium chloride to precipitate the whole of the oxalic acid, and after the addition of methyl-orange, to complete the titration. Ammonia may be titrated in the same way, preferably after the addition of boric acid to prevent loss by evaporation.[13]

The use of yellow mercuric oxide has also many advantages as an original standard, since it is readily obtained in a pure anhydrous condition and is not hygroscopic. When treated with a solution of potassium iodide, it yields an equivalent quantity of potassium hydroxide, and this is titrated with the acid to be standardised, using methyl-orange, methyl-red, or phenolphthalein as indicator.[14]

Alkalimetric methods of estimating phosphoric acids and alkali phosphates in admixture usually give only approximately correct results, but by maintaining the solution at 55° during each of the titrations, it is possible to estimate any of the alkali phosphates in a mixture with an accuracy within 0·5 per cent.[15]

In many cases methyl-red (*p*-dimethylaminoazobenzene-*o*-carboxylic acid) may advantageously replace methyl-orange as an

[9] G. Denigès, *Ann. Chim. anal.*, 1917, **22**, 127; *A.*, ii, 345, 419.
[10] Compare *Ann. Report*, 1916, 183.
[11] G. Bruhns, *J. pr. Chem.*, 1917, [ii], **95**, 37; *A.*, ii, 266.
[12] G. Bruhns, *ibid.*, 1916, [ii], **93**, 73, 312; *A.*, 1916, ii, 337, 581.
[13] G. Bruhns, *Chem. Zeit.*, 1917, **41**, 189; *A.*, ii, 270.
[14] G. Incze, *Zeitsch. anal. Chem.*, 1917, **56**, 177; *A.*, ii, 327.
[15] J. H. Smith, *J. Soc. Chem. Ind.*, 1917, **36**, 415; *A.*, ii, 330.

indicator, since it is more sensitive to hydrogen ions. It shows sharp end-points with oxalic acid, alkali borates, and cyanides, but is unsuitable for sulphites. With carbonates and sulphides, it produces intermediate colorations, and the titration must be continued until a bright pink tint is obtained.[16]

For the estimation of lime and magnesia in limestone, and for the analysis of ammonium salts, thymolphthalein has been found a useful indicator, owing to its not being sensitive to traces of alkali, even in boiling solutions.[17]

Further applications of differential iodometric methods have been described.[18] For the estimation of available oxygen in commercial permanganate and other oxidised forms of manganese which contain small amounts of iron, advantage is taken of the fact that ferric iron reacts so slowly with potassium iodide in phosphoric acid solution that it is possible by regulating the acidity of the solution to estimate iodometrically the available oxygen before the ferric iron reacts with the iodide.[19] The same principle may be used for the iodometric titration of chromic acid in the presence of ferric iron.[20] In the case of oxidised manganese ores containing a large proportion of ferric iron, this method is not trustworthy, but a suitable differential method of estimating the available oxygen has been based on the facts that on treating finely ground pyrolusite with hydrochloric acid and potassium iodide, liberation of iodine takes place; that ferric chloride in acid solution also liberates iodine, and that ferrous chloride is immediately oxidised by excess of iodine.[21] In another method of analysing pyrolusite, the finely divided sample is treated with potassium iodide, sodium phosphate, water, and phosphoric acid, and the liberated iodine titrated after about an hour.[22] On the whole, however, the ferrous sulphate and direct iodometric methods give the most trustworthy results in the evaluation of pyrolusite.[23]

The red coloration which is sometimes produced in the iodometric titration of hydrogen sulphide is probably due to hydrolysis of the starch indicator to erythrodextrin. No effective means

[16] F. Lehmann and G. Wolff, *Arch. Pharm.*, 1917, **255**, 113; *A.*, ii, 326.

[17] J. Moir, *J. Chem. Met. and Min. Soc. S. Africa*, 1917, **17**, 129; *A.*, ii, 386.

[18] Compare *Ann. Report*, 1916, 185.

[19] O. L. Barnebey and W. C. Hawes, *J. Amer. Chem. Soc.*, 1917, **39**, 607; *A.*, ii, 274.

[20] O. L. Barnebey, *ibid.*, 604; *A.*, ii, 274.

[21] O. L. Barnebey and G. M. Bishop, *ibid.*, 1235; *A.*, ii, 390.

[22] E. Rupp, *Arch. Pharm.*, 1916, **254**, 135; *A.*, ii, 390.

[23] O. L. Barnebey, *J. Ind. Eng. Chem.*, 1917, **9**, 961; *A.*, ii, 581.

of rendering the end-point of the reaction more definite has been found.[24]

For the iodometric estimation of cadmium in the presence of zinc, a convenient though somewhat slow method is to remove the zinc by crystallisation as sulphate. The solution containing the cadmium is then treated with hydrochloric acid and excess of $N/10$-iodine, and the remaining iodine titrated with thiosulphate.[25]

In estimating magnesium by Stolba's method of titrating the precipitate of magnesium ammonium phosphate with hydrochloric acid, it is essential that the solution should be neutral and that the ammonia should be added after the phosphate solution. The formation of the salt Mg_3PO_4 is prevented by keeping the solution just alkaline during the precipitation, and that of the salt $Mg(NH_4)_4(PO_4)_2$ by avoiding an excess of ammonium salts. For the accurate estimation of magnesium by precipitation as ammonium magnesium arsenate and iodometric titration of the precipitate, special precautions are also necessary. Thus a large excess of sodium arsenate must be used for the precipitation, whilst during the titration of the liberated iodine the solution must be kept decidedly acid to prevent a reverse action taking place. The solution must also be freed from ammonium salts.[26]

In another volumetric method, the magnesium is converted into magnesium oxalate by means of oxalic acid, the excess of which is titrated with alkali solution.[27]

The volumetric estimation of chromium in ferrochrome by the sodium thiosulphate and potassium dichromate methods is more accurate than by the permanganate method. With the latter, it is necessary to use the empirical value 0·3165 for chromium instead of the theoretical value 0·310.[28]

A trustworthy method of estimating molybdenum has been based on its reduction to Mo_2O_3 by means of hydrochloric acid and amalgamated zinc, the reduced solution being received in a vessel containing a chilled solution of iodine chloride in hydrochloric acid and titrated with standard potassium iodate solution. This rapidly oxidises the molybdenum to Mo_2O_5, the further oxidation to MoO_3 being negligible provided that care be taken to exclude direct sunlight.[29]

[24] A. R. Jayson and R. E. Oesper, *J. Ind. Eng. Chem.*, 1917, **9**, 975; *A.*, ii, 577.
[25] E. J. Ericson, *ibid.*, 671; *A.*, ii, 424.
[26] F. W. Bruckmiller, *J. Amer. Chem. Soc.*, 1917, **39**, 610; *A.*, ii, 271.
[27] N. Busvold, *Chem. Zeit.*, 1917, **41**, 42; *A.*, ii, 218.
[28] W. Herwig, *Stahl. u. Eisen*, 1916, **36**, 546; *A.*, ii, 104.
[29] G. S. Jamieson, *J. Amer. Chem. Soc.*, 1917, **39**, 246; *A.*, ii, 275.

Another volumetric method, particularly applicable to the estimation of molybdenum in steel, is to reduce the acidified filtrate from the iron with standard titanous chloride solution, the excess of which is then titrated with standard ferric chloride. If the solution does not contain more than about 0·05 gram per litre of molybdenum and more than about 1 per cent. of hydrochloric acid, the oxide MoO_3 is quantitatively reduced to Mo_2O_5. In like manner, the vanadium oxide V_2O_5 is reduced to V_2O_4.[30]

The principal source of error in the estimation of silica is the solution of the precipitate in hydrochloric acid, the amount dissolved varying with the proportion and strength of the acid, the temperature, and the time of contact. The most satisfactory method of dehydrating silica is to heat it for thirty minutes at 120° to 150°, and boiling the precipitate for three minutes with 60 per cent. hydrochloric acid usually gives as pure a silica as is obtained by longer boiling or the use of more concentrated acid.[31]

The low results obtained in certain cases in the estimation of nitrogen by Kjeldahl's method when mercury is added during the acid treatment[32] is due to the formation of mercury ammonium compounds, which are not subsequently decomposed. This source of error may be obviated by using potassium arsenite to decompose these compounds.[33] For the estimation of nitrogen in nitrates and nitrites, the solution may be distilled with magnesium chloride solution and a finely divided alloy of copper and magnesium, and the distillate collected in standard acid, the excess of which is titrated as in Kjeldahl's method.[34]

Under ordinary conditions, the precipitation of platinum sulphide is incomplete, owing to the formation of a stable colloidal solution, but by the addition of magnesium chloride, the hydrosol is converted into an insoluble hydrogel. A method of estimating platinum has been based on this fact, and gives results in close agreement with those obtained by electrolytic methods.[35]

A rapid method of separating iron from lead has been based on the insolubility of basic ferric nitrate, which is formed on evaporating the mixed salts with nitric acid and heating the residue at 100°.[36]

For the separation of iron from aluminium, advantage may be

[30] Travers, *Compt. rend.*, 1917, **165**, 362; *A.*, ii, 545.
[31] F. G. Hawley, *Eng. and Min. J.*, 1917, **103**, 541; *A.*, ii, 332.
[32] Compare *Ann. Report*, 1916, 187.
[33] E. Justin-Mueller, *Bull. Sci. Pharmacol.*, 1916, **23**, 167; *A.*, ii, 39.
[34] T. Arnd, *Zeitsch. angew. Chem.*, 1917, **30**, i, 169; *A.*, ii, 504.
[35] V. N. Ivanov, *J. Russ. Phys. Chem. Soc.*, 1916, **48**, 527; *A.*, ii, 154.
[36] J. F. Sacher, *Chem. Zeit.*, 1917, **41**, 245; *A.*, ii, 245.

taken of the fact that ferric chloride is soluble in ether, whereas hydrated aluminium chloride is insoluble in that solvent.[37]

The blue coloration formed when cobalt ammonium thiocyanate dissolves in amyl alcohol has long been known as a sensitive test for cobalt in nickel salts. It may also be used as a quantitative colorimetric method under specified conditions as to the concentration of the solutions, whilst by the addition of sodium pyrophosphate the formation of ferric thiocyanate is prevented, and no filtration is required.[38]

When hydrogen peroxide acts on a cobalt salt in the presence of ammonium chloride and ammonia, it forms a cobaltic ammonium salt which can be precipitated by ammonium molybdate, whereas nickel under the same conditions remains in the protoxide condition and is not precipitated by ammonium molybdate. On these facts, a new method of separating cobalt and nickel has been based. The presence of molybdate in the filtrate does not interfere with the precipitation of nickel by the dimethylglyoxime method.[39]

A satisfactory separation of nickel from copper may be effected by means of dimethylglyoxime, the solution being treated with sufficient potassium sodium tartrate to keep the copper in solution when the liquid is rendered alkaline for the precipitation of the nickel.[40]

Various discordant statements have been published as to the solubility of calcium carbonate in water. The discrepancy is due to the slow dissociation of the carbonate by boiling water, with the loss of carbon dioxide. This dissociation and solution may be prevented by the addition of a small amount of sodium carbonate, and advantage may be taken of this in estimating calcium in the form of carbonate. The precipitated carbonate is washed with boiling water containing a trace of sodium carbonate, is then dissolved in standard hydrochloric acid, and the excess of acid titrated with standard alkali hydroxide solution. The error due to sodium carbonate retained by the precipitate is negligible.[41]

Electrochemical Analysis.

The electrometric method of ascertaining the end-points of reactions in volumetric analysis, which has been shown to give good

[37] S. Palkin, *J. Ind. Eng. Chem.*, 1917, **9**, 951; *A.*, ii, 581.
[38] A. D. Powell, *J. Soc. Chem. Ind.*, 1917, **36**, 273; *A.*, ii, 220.
[39] A. Carnot, *Compt. rend.*, 1917, **164**, 897; *A.*, ii, 391.
[40] H. Grossmann and J. Mannheim, *Zeitsch. angew. Chem.*, 1917, **30**, i, 159; *A.*, ii, 512.
[41] A. Cavazzi, *Gazzetta*, 1917, **47**, ii, 49; *A.*, ii, 532.

results in the estimation of vanadates[42] and of vanadium and chromium in steel,[43] has now been utilised for other estimations. For example, in the titration of zinc with potassium ferrocyanide, advantage is taken of the difference of the *E.M.F.* of a platinum electrode when immersed in a solution of potassium ferrocyanide and in a solution of a zinc salt. The two electrodes (one of platinum wire and the other of calomel) are placed in the hot solution of the zinc salt, which is then titrated with the ferrocyanide solution until the pointer of the galvanometer, which, during the titration, has been slowly deflected from zero in one direction, swings sharply in the other direction on the addition of one drop in excess of the reagent. If more than a trace of cadmium is present, it must be removed prior to the titration.[44]

The method may also be used for the estimation of certain bivalent metals in solutions of their sulphates. Barium hydroxide is preferable to sodium hydroxide for the titration, since it shows a much sharper end-point. Accurate results are thus obtained in the estimation of copper, nickel, and cobalt, and the method may also be used for estimating magnesium in the presence of calcium, but is not applicable to cadmium, which appears to form a basic hydroxysulphate.[45]

Several methods have been devised in which substitutes are provided for platinum electrodes. For example, tin may be estimated in a hydrochloric acid solution of its salts by the use of a copper cathode and graphite anode,[46] whilst a copper cathode and an anode of passive iron may be used for the estimation and separation of zinc and cadmium.[47]

Platinum electrodes may also be replaced by silvered glass basins, a thin strip of platinum foil being bent over the edge of the basin to make the contact with the metal coating. Basins thus prepared may be used for the electrolytic estimation of copper, cadmium, zinc, nickel, and cobalt. After use, the coating is removed with nitric acid, and the basins resilvered.[48]

Another device to economise platinum has been adopted in a method of estimating manganese, which is deposited as manganese dioxide, from a solution of manganous sulphate, in which is

[42] G. L. Kelley and J. B. Conant, *J. Amer. Chem., Soc.* 1916, **38**, 341 ; *A.*, 1916, ii, 274.
[43] G. L. Kelley and J. B. Conant, *ibid.*, 719 ; *A.*, 1916, ii, 540.
[44] F. R. von Bichowsky, *J. Washington Acad. Sci.*, 1917, **7**, 141 ; *A.*, ii, 219.
[45] H. S. Harned, *J. Amer. Chem. Soc.*, 1917, **34**, 252 ; *A.*, ii, 272.
[46] T. Batuecas, *Anal. Fis. Quim.*, 1916, **14**, 495 ; *A.*, ii, 106.
[47] J. de Guzmán Carrancio and P. Poch, *ibid.*, 1917, **15**, 235 ; *A.*, ii, 509.
[48] J. Gewecke, *Chem. Zeit.*, 1917, **41**, 297 ; *A.*, ii, 334.

immersed a rotating anode of platinised glass. This is prepared by coating a tube of lead glass with a glycerol emulsion of chloroplatinic acid and heating the glass until it softens. The manganese dioxide is converted into manganous sulphate, which is dried at 450°, and weighed as the anhydrous salt.[49]

An electrolytic method for the evaluation of iron sulphide has been based on its decomposition with hydrochloric acid and zinc, and absorption of the evolved hydrogen sulphide in a solution of cadmium chloride. The precipitate is dissolved in hydrochloric acid, the cadmium precipitated by sodium hydroxide, the cadmium hydroxide dissolved in potassium cyanide solution, and the cadmium electrolytically estimated. The amount of sulphur corresponding with the cadmium thus separated is about 0·5 per cent. too low.[50]

Water Analysis.

For the removal of nitrites, the presence of which renders Winkler's[51] method of estimating oxygen in water untrustworthy, various methods have been suggested.[52] To these may be added a method of treating the water with concentrated carbamide solution and dilute sulphuric acid, the use of weaker solutions of the reagent causing the results to be too high. The trustworthiness of Winkler's method is increased by using sodium hydrogen carbonate for the conversion of the manganous hydroxide into manganous carbonate.[53]

Winkler's method of estimating carbon dioxide in water by titration with sodium carbonate solution[54] has been shown to be untrustworthy,[55] and its author has therefore recalculated the correction which must be applied to the results.[56] Precipitation of dissolved carbon dioxide or alkali hydrogen carbonate by means of barium hydroxide and titration of the excess of precipitant gives inaccurate results, owing to the precipitate containing occluded barium hydroxide. In the absence of magnesium salts, however, more trustworthy results may be obtained by titrating both liquid and precipitate together, using phenolphthalein as indicator.[57]

[49] F. A. Gooch and M. Kobayashi, *Amer. J. Sci.*, 1917, [iv], **44**, 53; *A.*, ii, 425.

[50] H. Williams, *Chem. News*, 1917, **116**, 13; *A.*, ii, 425.

[51] L. W. Winkler, *Zeitsch. anal. Chem.*, 1914, **53**, 665; *A.*, 1915, ii, 277.

[52] *Ann. Report*, 116, 191.

[53] H. Noll, *Zeitsch. angew. Chem.*, 1917, **30**, i, 105; *A.*, ii, 502.

[54] L. W. Winkler, *ibid.*, 1914, **53**, 746; *A.*, 1915, ii, 281.

[55] J. Tillmans and O. Heublein, *Zeitsch. Nahr. Genussm.*, 1917, **33**, 281; *A.*, ii, 332.

[56] L. W. Winkler, *ibid.*, 1917, **33**, 443; *A.*, ii, 423.

[57] J. Tillmans and O. Heublein, *loc cit.*

The presence of carbon dioxide in excess of 28 parts per million renders the results obtained by Blacher's method of estimating hardness in water [58] untrustworthy, but the amount may be readily reduced below that limit by aspiration. Sodium chloride in quantities up to 2000 parts per million has no appreciable influence on the results. It is essential, however, especially when the water contains both calcium and magnesium salts, that in the final titration the end-point should be taken when the phenolphthalein becomes intense pink, and not at the first sign of coloration.[59] For ascertaining the true neutralisation point of water, the use of methyl-red with α-naphtholphthalein gives more sensitive results than the mixture of methyl-orange and phenolphthalein ordinarily used as indicator. As little as 0·1 part of sulphuric acid or 0·2 part of calcium hydroxide in 100,000 parts of water may thus be detected.[60]

The accuracy of the usual method of titrating chlorine in water is increased by using a definite proportion of chromate solution (0·7 to 1 c.c. per 100 c.c. of water) as indicator. The presence of free acids, iron salts, or phosphates renders the method less sensitive, but borax has no influence on the results.[61]

An indirect method of estimating strontium gives trustworthy results provided that great care is taken to ensure the purity of the precipitates by reprecipitation. The weighed mixture of pure oxalates of calcium and strontium is dissolved in sulphuric acid, the solution titrated with standard permanganate solution, and the proportion of strontium calculated from the results.[61] Lithium also may be indirectly estimated by dissolving the mixed weighed chlorides of potassium, sodium, and lithium in water, and estimating the potassium and total chlorine in aliquot portions of the solution. From these results, the data are obtained for calculating the amount of lithium.[62]

The colorimetric method of estimating nitrates by means of phenoldisulphonic acid is rapid, but involves several possible sources of error. For example, if chlorides are present, the addition of sulphuric acid to the dry residue produces heat, which causes chlorine and nitric acid to be liberated. This may be prevented by adding the sulphuric acid prior to evaporation of the mixture to a small residue, but not to dryness. It is preferable that the

[58] C. Blacher, P. Grünberg, and M. Kissa, *Chem. Zeit.*, 1913, **37**, 56; *A.*, 1913, ii, 153.

[59] A. S. Behrman, *Philippine J. Sci.*, 1916, **11**, [A], 291; *A.*, ii, 542.

[60] J. Moir, *J. Chem. Met. and Min. Soc. S. Africa*, 1917, **17**, 129; *A.*, ii, 386.

[61] I. M. Kolthoff, *Pharm. Weekblad*, 1917, **54**, 612; *A.*, ii, 379.

[62] S. D. Averitt, *J. Ind. Eng. Chem.*, 1917, **9**, 584; *A.*, ii, 423.

temperature during the evaporation should not exceed 70°, and if the proportion of chlorine is very high, evaporation under diminished pressure is advisable. It is also essential for accurate results that the proportion of nitrates to reagent should fall within definite limits.[63] In the case of waters rich in magnesium salts, a turbidity due to magnesium hydroxide is produced on neutralising the acid liquid. The addition of ammonium chloride will prevent this precipitation, but if iron is also present, the neutralised liquid must be filtered before making the colour comparison.[64] A simple method of removing nitric acid from sulphuric acid for use in this test is to shake the acid with mercury in a Lunge's nitrometer.[65]

C. Ainsworth Mitchell.

[63] W. F. Gericke, *J. Ind. Eng. Chem.*, 1917, **9**, 585; *A.*, ii, 421.
[64] M. S. Nichols, *ibid.*, 1917, **9**, 186; *A.*, ii, 421.
[65] H. D. Steenbergen, *Chem. Weekblad*, 1917, **14**, 647; *A.*, ii, 421.

PHYSIOLOGICAL CHEMISTRY.

Progress during the past year seems to have been made chiefly on certain special lines. I have dealt with some of these rather fully, and have therefore grouped my remarks under comparatively few headings.

The Alkaline Reserve of the Body.

The myriad chemical reactions which in the living body together constitute 'metabolism' can progress normally only when certain general conditions are steadily maintained. Normality of temperature, osmotic pressure, and hydrion concentration in the fluids and tissues is essential to the normality of metabolism as a whole, and the permissible range of variation is surprisingly small, especially in the case of the factor last mentioned. The existence of mechanisms to secure, automatically, a fine adjustment in hydrion concentration is a striking characteristic of the physiological machine. To our knowledge of these physiological and chemical mechanisms the work of the last few years has brought new and satisfactory precision. The acquirement of this on the physiological side may be said to have begun when it was shown how exceedingly sensitive is the respiratory centre to changes of carbon dioxide tension,[1] or, as very soon became clear, to any change in hydrion concentration.[2] With even the most minute increase in this there is stimulation of the centre with a consequent increased elimination of carbon dioxide through the lungs, and so an automatic return towards the normal. If, however, the lungs, as controlled by the respiratory centre, were solely responsible for the regulation, the animal could certainly not display the relatively equable rhythm of respiration which is characteristic of normal life. The sensitiveness of the kidney epithelium to fluctuations in C_H provides a second physiological regulatory mechanism which is constantly in action. The organ promptly excretes hydrions when they are in excess. Associated with the

[1] J. S. Haldane and J. G. Priestley, *J. Physiol.*, 1905, **32**, 225; *A.*, 1905, ii, 400.

[2] C. Lunsgaard, *Biochem. J.*, 1912, **41**, 247.

physiological mechanisms are chemical means for regulation, and these, in normal circumstances, are sufficient to spare the former from having to deal with more than minor fluctuations. The buffer salts of the blood and the possibility of certain metabolic readjustments form a first line of defence against gross changes of reaction. Our knowledge with regard to these has recently gained greatly in clearness largely owing to the work of L. J. Henderson [3] and to the researches which his writings have stimulated. The chemical determinants of hydrion equilibrium in the blood are the carbonates, the phosphates, and the proteins contained in it. Henderson has made it clear that of these the carbonates play by far the most important part; in the plasma, indeed, almost an exclusive part. An aqueous solution of about 0·12*N*-sodium hydrogen carbonate exposed to a proper tension of carbon dioxide will, in respect to the changes in C_H produced by adding varying amounts of acid, serve as a simple model of the plasma.[4] A determination in the plasma of the ratio $H_2CO_3/NaHCO_3$ may, as Hasselbalch [5] has shown, give even a better measure of the C_H than any obtained by the gas-chain method.

Intimately related to the actual hydrion concentration, but requiring separate consideration, is the "alkaline reserve" of the blood and tissues. Any appreciable change in the former only occurs in the blood under conditions of extreme abnormality, but two individuals displaying at any moment a normal blood reaction, and both therefore free from the symptoms which follow on a disturbance in that reaction, may yet be in very different metabolic positions. In one the alkaline reserve may be untouched and normal; in the other it may be near exhaustion and the individual in danger.

"Free carbonic acid is present in the body fluids in such concentration that it automatically converts into bicarbonate all bases not bound by other acids. *The bicarbonate therefore represents the excess of base* which is left after all the non-volatile acids have been neutralised, and is available for the immediate neutralisation of further acids. In this sense it constitutes the *alkaline reserve of the body*. The bicarbonate concentration of the blood is representative of that of the body fluids in general, and is normally maintained at a definite level. Entrance of free acids reduces it to an extent proportional to the amount of the invading acid." It is found that plasma obtained by drawing blood from a vein of the arm contains at 37° and normal carbon dioxide tension approximately 60 vols. per cent. of carbon dioxide bound as bicarbonate.

[3] Compare *J. Biol. Chem.*, 1911, **9**, 403; *A.*, 1911, ii, 752. *Ergebn. Physiol.* 1909, **8**, 254.

[4] K. A. Hasselbalch, *Biochem. Zeitsch.*, 1916, **78**, 112; *A.*, i,490.

[5] Not of the blood, as implied by Michaelis ("Die Wasserstoffionen-Koncentration, Berlin, 1914).

This means that, with the average tension in arterial blood (42 mm.), the ratio of unbound to bound carbon dioxide (H_2CO_3/$NaHCO_3$) = 1/20. If abnormal quantities of acid enter the blood, the organism is able, until a large part of its bicarbonate reserve has become exhausted, to maintain by accelerated respiration the above ratio at its normal value. The C'_H being, as we have seen, proportional to this ratio, also remains normal.

It is clear that quantitative knowledge concerning the available bicarbonates is desirable both in physiology and pathology. Important contributions to the technique of estimations and a number of valuable data have been published during the year from the Rockefeller Institute for Medical Research in a series of papers by D. D. van Slyke and his co-workers. In a preliminary paper,[6] from which I have already quoted, the considerations briefly sketched above are fully and clearly dealt with. Various methods which have hitherto been used for the detection of acidosis are reviewed and shown to be essentially means, sometimes rough or approximate, for the estimation of bicarbonates. Much experimental work is also described dealing with points which needed investigation before the method described in the second paper[7] could be critically applied to the problem. In this method a special form of apparatus is used which permits of an estimation of bound and unbound carbon dioxide on very small quantities of blood, such as can be withdrawn without inconvenience from human subjects. The apparatus is essentially simple, and its description is likely to stimulate in the immediate future valuable work from the hands of many observers. Illustrating the present tendency in biochemistry to strive after accurate micro-analytical methods is the further description of a modification of the apparatus which measures within one volume per cent. the small amount of carbon dioxide (0·1—0·15 c.c.) contained in 0·2 c.c. of blood plasma, a quantity which can be obtained on pricking the finger. Technical points which arise in connexion with the use of either form of apparatus are fully discussed, and tables are supplied which simplify the calculations.

The ideal method for determining the alkaline reserve is to estimate the bicarbonate in arterial blood when exposed to the particular tension of carbon dioxide actually existing in the vessels of the subject or patient, as measured, for instance, by the alveolar tension in his lungs. In routine work it is sufficient to use the easier experimental conditions offered by the use of venous blood previously exposed (in apparatus described in the paper) to the

[6] D. D. van Slyke and G. E. Cullen, *J. Biol. Chem.*, 1917, **30**, 289; *A.*, i, 521.

[7] D. D. van Slyke, *ibid.*, **30**, 347; *A.*, ii, 422.

normal mean tension. The results are equally definite in their significance.

The third paper [8] in the series under review deals with the electrometric titration of plasma as a method of measuring its alkaline reserve. This can be carried out on much smaller quantities of blood than ordinary titration would require, and gives much sharper end-points. The well-known gas-chain method with calomel cells was used, every precaution being taken to secure the highest grade of accuracy. A definite amount of standard acid was added to a measured volume of plasma on the assumption that the resultant change in C_H will be greater the less the alkaline reserve. Since the initial reaction of all plasmas is practically constant, and since, as direct observations showed, the curve of titration got by adding successive amounts of acid is almost a straight line, the claim is made that it is possible to construct a curve from one determination, and from it to determine the amount of acid required to bring the plasma to any desired reaction. To obtain comparable results it is necessary to bring all samples to a definite carbon dioxide content. Two procedures were adopted: the plasma was either first shaken with a known volume of air and an equal volume of $N/50$-hydrochloric acid then added, or of acid sufficient to liberate all the carbon dioxide from the carbonate (two volumes of $N/50$) was first added and the carbon dioxide then removed. In each case the acidified plasma was transferred to a Clark electrode and the resultant C_H determined. The results obtained by the two methods were, of course, not identical, but they were found to run parallel under varying conditions. Experiment showed that the hydrogen exponent (Sörensen) of plasma when mixed with 1 volume of $N/50$-acid becomes, in the case of normal human blood, 7·00. When two volumes of $N/50$-acid are added it becomes 5·6. These are average figures, certain fluctuations occurring during the day. In extreme cases of diminished alkaline reserve exponents were obtained as low as 5·7 after the addition of one volume of acid, and of about 4·8 after adding two volumes.

The renal mechanism is, as I have already pointed out, continuously concerned with the adjustment of C_H in the blood. It is of great interest, therefore, to know how far quantitative relations can be shown to exist between the production of acid in metabolism and the rate of excretion of hydrogen ions, or, in other terms, between the existing alkaline reserve and the contemporary excretion of acid.

In last year's Report the formula of Ambard and Weil was briefly discussed. This empirical formula professes to relate the

[8] G. E. Cullen, *J. Biol. Chem.*, 1917, **30**, 369; *A.*, i, 521.

concentration of substances in the circulation with their concentration in the urine and with the rate of their elimination. With some reservations it may be said to hold satisfactorily in the case of urea and chlorides. Does it obtain in the case of acids? In the fourth paper [9] of the series under review we are given experimental evidence which suggests that it does.

Ambard and Weil's formula may be put in the form $C^b = k \times \sqrt{D/w}\sqrt{C^u}$, where C^b is the concentration of the substance in the blood *above* the *excretion threshold*, C^u its concentration in the urine, and D the rate of its excretion; and w is the body weight.

Before any attempt to decide as to how far acid excretion follows this law, certain considerations must be borne in mind. In the first place a great part of whatever acid is produced in metabolism in excess of available mineral bases is neutralised by ammonia. In the second place it must be noted that C^b in the above equation refers to concentration in excess of a certain threshold value, and in the case of acid we need some definition for this value. Experiments show that the acidity of urine titrated (by Folin's method) with phenolphthalein as indicator, approaches zero when the concentration of the blood bicarbonate corresponds with 80 volumes per cent. of carbon dioxide. In these circumstances the excretion of ammonia also approaches zero.

In applying Ambard's formula to the excretion of acid, D was therefore made to represent the rate of excretion of $N/10$-acid, plus ammonia, for a twenty-four hour time unit, and C^u became the number of c.c. of $N/10$-acid, plus ammonia, per litre of urine. On the assumption that acid accumulation in the blood is proportional to the fall in carbon dioxide below 80 vols. per cent., the relation between the blood accumulation and acid excretion becomes:

$$\text{Retained acid} = 80 - \text{observed } CO_2 \text{ of plasma} = \text{constant} \times \sqrt{D/w} \,.\, \sqrt{C^u}.$$

The constant proved to be unity, so we have:

$$\text{Plasma } CO_2 \text{ capacity} = 80 - \sqrt{D/w}\sqrt{C^u}.$$

It should be understood that the formula, although suggested by the researches of Ambard and Weil, is wholly empirical, and was employed solely because no other expression fitted the experimental results so well. The margin of error found, when results calculated from the formula were compared with direct determinations of the carbon dioxide bound in plasma, was about 10 volumes per cent. Of thirteen observations made on normal individuals, some of whom were given bicarbonate by the mouth, eight showed an error of less than four volumes per cent. The average of the deter-

[9] R. Fitz and D. D. van Slyke, *J. Biol. Chem.*, 1917, **30**, 389, *A.*, i, 522.

minations was 71·3 c.c. of carbon dioxide per 100 c.c. plasma, the average of the calculated results was 71·6.

In a fifth paper [10] figures are given for the quantitative relation which obtains between the alveolar carbon dioxide tension and the co-existing plasma bicarbonate. The former was determined by Fredericia's modification of Haldane's method, and the latter by van Slyke's method as described above. The range of plasma carbon dioxide was found to be between 53 and 75 c.c. bound as bicarbonate. Gettler and Baker,[11] using essentially the same method, found the range in thirty individuals to be between 56 and 78 c.c. The extreme range for normal adults may now be looked on as established, being from 53 to 78 c.c. The ratio—plasma CO_2/mm. alveolar CO_2—varies from 1·27 to 1·80, the average value being about 1·5. Approximate information as to the existing alkaline reserve may be obtained therefore by multiplying the observed alveolar tension by the latter figure. The variations must not be forgotten, however. It has been found that digestive activity causes a rise in alveolar carbon dioxide tension, and the fact has been explained on the one hand [12] as being due to an increase in the reserve alkali of the blood, caused by the secretion of hydrochloric acid in the gastric juice; on the other hand,[13] as a change in the irritability of the respiratory centre. The occurrence of this rise is confirmed in the present research, and the experiments described favour on the whole the latter explanation.

The main purpose of the series of researches just discussed was to make it possible to determine the relationship of the blood bicarbonate as directly estimated to that estimated indirectly from the excretions of the lungs and kidneys. The sixth and last paper [14] describes the application of the various methods to a number of cases of diabetes. The indications given by the methods were thus compared, whilst data were obtained as to the relationship of plasma bicarbonate deficiency to the clinical severity of acidosis. In twenty-one cases the alveolar tension of carbon dioxide, the bicarbonate of the whole blood and of the plasma, the hydrogen-ion concentration, and the index of acid excretion were all determined. Curves are given in the paper which show the variation in these factors from day to day. On the whole, the curves are remarkably parallel. The alveolar tension in diabetic patients under treatment is, how-

[10] D. D. van Slyke, E. Stillman, and G. E. Cullen, *J. Biol. Chem.*, 1917, **30**, 401 ; *A.*, i, 523.

[11] A. O. Gettler and W. Baker, *ibid.*, 1916, **25**, 211 ; *A.*, 1916, i, 576.

[12] H. Erdt, *Deutsch. Arch. Klin. Med.*, 1915, **47**, 497.

[13] H. L. Higgins, *Amer. J. Physiol.*, 1914, **24**, 114 ; *A.*, 1914, i, 613.

[14] E. Stillman, D. D. van Slyke, G. E. Cullen, and R. Fitz, *J. Biol. Chem.*, 1917, **30**, 405 ; *A.*, i, 523.

ever, often much too low to indicate the true level of the blood bicarbonate, although in severe acidosis this discrepancy disappears. On the other hand, the consistent agreement of the figures for plasma carbon dioxide directly determined and those calculated as above from the index of acid excretion by the kidney is striking, and certainly very interesting. Only when bicarbonate is being given by the mouth or when the acidosis is very severe, does this agreement fail. Of the two indirect measures of alkaline reserve that given by the lungs appears to be more trustworthy when the reserve is very low and coma threatened, whilst that given by the kidney is to be preferred in the more common intermediate stages. The results point to the following relations between the degree of acidosis and the bound carbon dioxide in 100 c.c. of the plasma: normal adult, 77—53; mild acidosis, 53—40; moderate acidosis, 40—30; severe acidosis with definite symptoms of acid intoxication, below 30. The lowest volume of plasma carbon dioxide recorded in which recovery occurred is 16. It may be noted that, as pointed out in the first paper of the series, there is at present confusion in the literature with respect to the term acidosis. Different authors regard acidosis as "acid intoxication," as a condition in which acetone substances are formed, or as an actual increase in the hydrogen-ion concentration in the blood. It is here defined as a condition in which the concentration of bicarbonate in the blood is reduced below the normal level. In cases where C_H is actually increased, the term "uncompensated acidosis" has already been employed. It is now proposed to speak of "compensated acidosis" when, despite decreased bicarbonate, the respiratory mechanism succeeds in keeping the ratio $H_2CO_3/NaHCO_3$, and therefore the C_H, within normal limits.

A special form of apparatus for gas analysis also applicable to the determination on small amounts of material of the free and combined carbon dioxide in blood or serum has been described by Y. Henderson and W. H. Morriss.[15] Their paper contains values obtained from the blood of patients in the gynæcological wards of the Yale School of Medicine. Van Slyke's method was compared with that of the author's, and the results were consistent. J. F. McClendon[16] and his co-workers have published diagrams by means of which the alkaline reserve may be ascertained when either the alveolar carbon dioxide tension, the total carbon dioxide of the serum, or its C_H under known tensions of carbon dioxide has been determined.

[15] *J. Biol. Chem.*, 1917, **31**, 217; *A.*, ii, 506.

[16] J. F. McClendon, A. Shedlov, and W. Thomson, *ibid.*, 1917, **31**, 519; *A.*, **i**, 671.

It will have been noticed that the researches described in the foregoing paragraphs have for the most part been carried out with plasma or serum and not with the whole blood. The use of either of the two former adds greatly to the ease of estimations, and there would seem to be sufficient evidence to show that the plasma bicarbonate is a real index of the alkaline reserve of the whole blood and of the tissues. It is an index because there exists an acid-base equilibrium between corpuscles and plasma and between blood and tissues, which on the occurrence of any change is rapidly readjusted.

Moreover, when we speak of the reaction of the blood we refer, strictly speaking, to the reaction of its plasma. It is this which is measured by an electrode immersed in the whole blood; the corpuscles merely remain suspended indifferently in the fluid, and may be removed without altering the *E.M.F.* reading. Doubtless, moreover, it is the reaction of the plasma which comes into direct contact with the tissues that is of importance physiologically. When corpuscles and plasma are in equilibrium under any given conditions, the removal of the former will produce no change in the ionic equilibrium provided that the conditions remain unchanged. Towards a *change* of conditions, however—of carbon dioxide tension, for example—the separated plasma will behave differently from the whole blood, because the corpuscles play so considerable a part in determining the equilibrium condition.[17]

To understand the behaviour of the whole blood when, for instance, carbon dioxide or other acids enter it as they arise in metabolism, we must take account of the corpuscles. We must do so, indeed, if we are considering the actual alkaline reserves of the blood.

It was long ago shown[18] that with increasing carbon dioxide tension, hydrogen chloride (or rather the chlorine ion) leaves the plasma for the corpuscles; and a recent paper[19] contains evidence to show that the SO_4 ion does the same. Apparently under the same conditions, potassium and sodium also leave the corpuscles. Thus increasing tension of carbon dioxide increases the alkalinity of the plasma, and reverse changes follow with diminishing tension. Hasselbalch[20] has directly shown that the P_H of the whole blood, that is, of the plasma in contact with corpuscles (see above), changes much less with changes of tension in carbon dioxide than does that of plasma, serum, or simple solutions of bicarbonate. Hasselbalch

[17] Compare T. R. Parsons, *J. Physiol.*, 1917, **51**, 440.
[18] Gurber, *Sitzungsber. physik. med. Ges. Würzburg*, 1895, 21.
[19] S. de Boer, *J. Physiol.*, 1917, **51**, 211; *A.*, i, 671.
[20] K. A. Hasselbalch, *Biochem. Zeitsch.*, 1916, **78**, 112; *A.*, i, 490.

does not attribute this simply to the influence of the corpuscles as representing a separate phase across the surface of which ionic interchanges occur, or to the real, if minor, influence of the phosphates within the corpuscles, but rather to the special influence of oxyhæmoglobin as an ampholyte. This substance becomes the more acid the more alkaline the reaction of its milieu. It acts as buffer to a degree of which the plasma proteins are incapable and promotes decomposition of bicarbonates during diminishing tensions of carbon dioxide. The properties of hæmoglobin in this connexion are of physiological importance, since, when the blood is taking up carbon dioxide from the tissues, the oxyhæmoglobin becomes reduced, and reduced hæmoglobin is less acidic.

As a result of observations involving ingenious technique and made partly in continuance of interrupted work by R. A. Peters, T. R. Parsons [21a] has shown that the I'_{H} of fully oxygenated blood at a given tension of carbon dioxide is less than that of completely reduced blood by 0·038, and that the difference between arterial and venous blood is approximately 0·02. The effect of oxygen in expelling carbon dioxide from the blood is due to the increase of acidity it produces. The author claims that changes in the relative number of corpuscles to the extent actually observed in pathological conditions exerts an appreciable effect on the reaction of the blood in the body, and so on the respiratory equilibrium.

Some Aspects of Nutrition.

The present shortage in the food supply of the world makes important every detail of knowledge concerning human nitrition. Even facts which seem academic need scrutiny, in case at some point or other they may find application in the direction of guidance for economy. In the present section I shall consider together, without much regard to order, the results of a number of recent researches into various aspects of nutrition.

Particularly desirable just now is any scrap of knowledge concerning the cereals. Except in arctic climates, bread and cereals are always important items in the food of mankind, and except where wealth has accumulated and luxury come in its train, they are by far the most important. Circumstances have to be very exceptional indeed when the growing of cereals does not yield an energy supply for the worker at less cost and with less relative effort than any other method of food production. Economic and social factors usually tend to make bread by far the most convenient form in which the cereals can reach the individual consumer.

[21a] *Loc, cit.*

The nations of the West have acquired the habit of demanding a well-piled loaf, and for this the special properties of wheat gluten seem necessary. Hence the reliance on wheat in the West. Yet it has been calculated that, after all, no more than a fourth of mankind relies on wheat, and when a relative shortage in this cereal renders it desirable that other cereals should accompany it in bread, the consequences should not be prejudged.

Experiments on animals show, indeed, that wheat when compared with other grains has no outstanding merits as a nutrient. No cereal forms a perfectly balanced food when eaten to the exclusion of everything else; but except of milk, and of that only as a food for infants, the same may be said of every other individual foodstuff. In countries like Australia, where wheat is especially abundant, efforts to use it instead of oats for working horses, and to employ it largely in the raising of stock, have resulted in relative failure. A ration wholly from the wheat plant—grain plus straw—when fed to heifers has been shown to be entirely inadequate for reproduction, and in some instances even for continued growth.[21]

Pigs when given wheat alone, even although certain mineral deficiencies in the grain are made good, soon cease to grow and develop pathological symptoms, proving wheat, in this particular case, to be inferior to maize.[22] To remedy completely the deficiencies displayed, it would seem that not only must the balance in mineral salts be improved and accessory factors of the vitamine type be increased in amount, but the protein of the grain must be improved by the addition of other proteins. It is claimed that part of the symptoms displayed by animals on an exclusive wheat dietary containing the whole grain are due to a toxic factor.[23] I am not quite sure that the evidence for this view is yet sufficient. Still further observations of a quantitative sort involving the adjustment of deficiencies seem first called for. Nevertheless, an oil with definitely toxic properties has been extracted from the wheat embryo.

It may be noted that some inherent deficiency in a diet may not be fully disclosed until animals fed on it are allowed to breed. Complete failure to rear young may characterise an abnormal state of nutrition which is not obvious in the parent

[21] E. B. Hart, E. V. McCollum, and G. C. Humphrey, *Exp. Stat. Research Bull.*, 17 (1911).

[22] E. B. Hart, and E. V. McCollum, *J. Biol. Chem.*, 1914, **19**, 373; *A.*, 1914, i, 620.

[23] E. B. Hart, W. S. Miller, and E. V. McCollum, *ibid.*, 1916, **25**, 239; *A.*, 1916, i, 581.

animal itself. This failure seems to be generally exhibited by animals on an exclusive wheat diet.[24]

Agriculturists have long recognised the inadequacy of maize as a sole diet for animals. This inadequacy is due to various causes. When it is fed to working horses, the effect of a relative excess of carbohydrate and deficiency of total protein makes itself felt. In the case of growing animals, mineral deficiency and errors in the amino-acid balance of its proteins have to be recognised. Recent researches have given us a more accurate analysis of these various deficiencies. Apparently, whilst one of them is the more important to one kind of animal, another may be of greater moment to another species. For example, the mineral deficiencies of maize are tolerated much better by pigs than by rats; its protein deficiencies, on the other hand, are borne more readily by the latter.[25] Such differences, however, are only relative. Pigs, for instance, when fed on maize-meal, fortified by the addition of extra proteins derived from maize itself, showed little or no growth, but when suitable salts were added, approximately normal growth was observed.[26] Nevertheless, on this diet perfectly normal reproduction could never be obtained. Young were born, but the mother failed to rear them.[27] Maize, like other grains, is quantitatively deficient in a factor to which I shall later make further reference, the substance called "fat soluble A" by McCollum. Animals thrive better on maize diet when an extra supply of this is given in natural butter or in the form of an alcoholic extract derived from maize itself. Some particularly interesting data concerning maize as a foodstuff have been published by A. G. Hogan.[28] His experiments confirm the generally accepted view that the chief mineral deficiency is one of calcium. The low nutritive value of the proteins is shown strikingly in experiments with pigs. Thus one set of animals of which the protein supply was wholly in the maize showed an average gain in weight, in 780 days, of only 5 kilos. Another set of which the diet was the same but for a small addition of casein (1·22 per cent. of the whole ration and about 10 per cent. of the whole protein) gained in the same time an average of 81 kilos. The vast superiority of casein as a protein for growth is obvious. The nature of the deficiency in the protein was brought out in experiments on rats. These experiments,

[24] E. V. McCollum, N. Simmonds, and W. Pitz, *J. Biol. Chem.*, 1916, **28**, 211; *A.*, i, 184. Hart, McCollum, and Humphrey, *loc. cit.*

[25] A. G. Hogan, *J. Biol. Chem.*, 1916, **29**, 193; *A.*, 1916, i, 861.

[26] E. B. Hart and E. V. McCollum, *ibid.*, 1914, **19**, 373; *A.*, 1915, i, 39.

[27] E. V. McCollum, N. Simmonds, and W. Pitz, *ibid.*, 1916, **28**, 153; *A.*, i, 192.

[28] *J. Biol. Chem.*, 1917, **29**, 485; *A.*, i, 363.

whilst chiefly confirmatory of previous work by others, gave particularly clear results. The whole proteins of maize, and zein alone, were supplied in the basal dietary. On this diet the animals were not maintained. The addition of lysine alone led to no improvement, but added tryptophan greatly improved the condition. When both these amino-acids were added, health and growth became normal. Tryptophan, therefore, is the first limiting factor in the nutritive value of maize proteins, but when this is supplied, lysine proves to be a second limiting factor.

It seems probable that in the case of oats the nutrient factors are, from the point of view of the animal, better balanced than is the case in either wheat or maize. Many observers, it is true, have reported failure in attempting to keep animals in health on oats alone. In the case of rabbits, the symptoms which appear have been ascribed to simple acidosis, as they are prevented by the administration of sodium hydrogen carbonate.[29] This observation has been recently confirmed.[30] In guinea-pigs, however, a more serious condition develops, for, as is well known from the original experiments of Holst and Frohlich,[31] an exclusive oat diet, no less than one consisting solely of other grains, induces symptoms in these animals which are indistinguishable from those of scurvy. These animals placed on a grain dietary have been much used, therefore, to demonstrate the presence of anti-scorbutic factors in various foodstuffs. The results obtained, both in the way of prevention and of cure, have seemed striking enough. Doubt, however, has been recently thrown on the view that scurvy is really a "deficiency disease." E. V. McCollum and W. Pitz[32] claim to have shown that the symptoms, in the guinea-pig at any rate, are due, not to the absence of an anti-scorbutic vitamine, but simply to a retention of material in the cæcum, owing to the unfavourable physical character of the diet. This leads to bacterial poisoning. The symptoms, according to these authors, can be prevented by the administration of substances which depress the growth of micro-organisms in the digestive tract or which facilitate the elimination of the fæces. I have read their paper without being convinced that their case is established. The experimental results are very irregular, and in this respect, unlike those obtained by others who have used fresh vegetables or fruit juices for prevention or cure.[33]

[29] A. Morgen and C. Beger, *Zeitsch. physiol. Chem.*, 1915, **94**, 324; *A.* 1915, i, 922. [30] C. Funk, *J. Biol. Chem.*, 1916, **31**, 229; *A.*, i, 696.
[31] *J. Hygiene*, 1907, **7**, 634.
[32] *J. Biol. Chem.*, 1917, **31**, 229; *A.*, i, 604.
[33] A. Holst, *J. Hygiene*, **7**, 619; Harriette Chick and Margaret Hume, *Trans. Soc. Trop. Med. and Hygiene*, 1917, **10**, (8), 141.

It is very hard to believe, moreover, that the remarkable appearance of anti-scorbutic power in grains and seeds at the moment of germination could depend on an acquirement of laxative or eliminative properties.[34] Nevertheless, the observations of McCollum and Pitz must be carefully borne in mind in any future work on this subject. Funk,[35] strange to say, has found that the guinea-pig, when on an oat diet, is but little protected by the administration of anti-scorbutics; the only fresh products he used, however, were milk and potato juice. He found the former to be the more efficacious of the two, a result which does not agree with the observations of others.[36]

Reviewing what has been said of the various cereals, it will, I think, be admitted that what we know of their nutritive properties from animal experiments does not suggest that wheat takes any pre-eminent position. As any one of the cereals proves when eaten alone to make an ill-balanced dietary, it is likely that admixture of two or more may actually improve the balance of nutritive elements in bread.

Another question arises in connexion with grain foods which is of great practical importance at the present time. What is the effect of increasing the percentage extraction of grain on the nutritive value of flour and bread? Do we gain by such an increase, or does the small digestibility of the added fraction nullify such gain? I need only refer to the report of the Royal Society Food (War) Committee on this subject. Careful and sufficiently prolonged digestibility experiments on twelve individuals, comparing a bread made from wheat flour of approximately 80 per cent. extraction with one made from 90 per cent. flour, showed, in spite of a slightly lessened digestibility, a marked gain in actual nutriment when the latter was employed—a gain in available energy equal to something like a month's supply of cereal food for the nation. An interesting point shown by these experiments is the great uniformity displayed by individuals in the power of digesting a dietary. Of the total calories contained in the diet comprising the 80 per cent. bread, 96·14 per cent. were on the average digested. The extreme departures from this were 95·1 per cent. in one case and 96·96 in another. The average agrees closely, moreover, with that obtained in experiments made at Cambridge some years ago with four quite different individuals.[37] On a closely similar but not identical bread, the calories digested were

[34] **Fürst,** *Zeitsch. Hygiene*, **1912, 72,** 121.
[35] C. **Funk,** *J. Biol. Chem.*, 1916, **25**, 409; *A.*, 1916, i, 696.
[36] **H. Chick and M. Hume,** *loc. cit.*
[37] *J. Hygiene*, **1912, 12,** No. 2, 119.

97·27 per cent. of the whole. In the Royal Society's experiments, the diet containing bread made from the flour of higher extraction showed on the average a digestibility (in respect of its calories) of 94·5 per cent. Such figures show how little basis has the not uncommon belief that even the present-day Government regulation flour (80 per cent.) has qualities which lead to a serious wastage of its food value.

Miss Harriette Chick and Miss Margaret Hume have, in very thorough experiments, studied the precise distribution of the anti-neuritic vitamine in the grains of wheat, rice, and maize. Pigeons were fed on a basal daily ration of about 2·6 grams of polished rice. On this alone the birds usually develop symptoms of neuritis in from fifteen to twenty-five days. The various parts of the grain were tested either as preventitives, when they were added to the rice from the beginning of the experiment, or as curative agents by administration after the symptoms had developed. It was found that in all the grains the vitamine is concentrated mainly in the germ or embryo, and that it is present to a less degree in the bran (pericarp and aleurone layer), probably more particularly in the aleurone layer.

As the subject of vitamine has received a good deal of attention in recent Reports, I had, as a matter of fact, intended to omit it here, thinking further reference to it might await the arrival of real knowledge as to the nature of these substances. The work of the year has rather forced my hand, however.

It was to be expected that conceptions new and foreign to views long held would have to submit to a period of criticism. I have just dealt with doubts thrown on the hypothesis of anti-scorbutic vitamines, although these doubts proceed from authors who strongly believe (and whose own work deeply commits them to the belief) in the part played by vitamines when growth and the maintenance of general nutrition are in question.

F. Röhmann,[38] however, has lately published in Germany a brochure in which the importance of such factors is repudiated. This publication I have myself been unable to obtain, but it is quoted and dealt with in a recent paper by Osborne and Mendel.[39] Röhmann asserts that "accessory foodstuffs are, at any rate, not necessary for the continued maintenance of full-grown animals." In this he may be right if by "continued maintenance" he means maintenance for somewhat long, although by no means indefinite periods. He goes further, however, and expresses the belief that

[38] F. Röhmann, "Ueber Künstliche Ernährung und Vitamine," Berlin, 1916.

[39] T. B. Osborne and L. B. Mendel, *J. Biol. Chem.*, 1917, **31**, 149; *A.*, i, 603.

the long familiar factors of energy, protein, salts, etc., if properly adjusted, suffice for the growth of the young animal and for all purposes. Osborne and Mendel, in the paper referred to, have criticised the comparatively few experiments on which Röhmann apparently relies for proof that animals (mice) can grow and ultimately produce young on pure synthetic dietaries. The food preparations used seem to offer quite insufficient guarantees that vitamines were absent from them. For my part, I am convinced from a careful re-perusal of all the published evidence, as well as from my own experiments, that the existence of factors of unknown nature, present in most natural foodstuffs, essential to growth, and active in very small concentration, is now proved. As to how they exert their effect, whether by directly stimulating the growing tissues, or, as is possible, along lines much more indirect, we are wholly ignorant. I have said that the vitamines are substances of unknown nature, but if one return for a moment to the anti-neuritic agent or agents (which are not necessarily the same as the growth factors), reference should, I think, be made to the truly remarkable statements of R. R. Williams. This author has found that certain pyridine derivations exist in two isomeric forms of different stability. In the case of 2-hydroxypyridine, for instance, there is an unstable form crystallising in needles and a stable form crystallising differently. Now the first form (which has probably a betaine structure), but not the second, is said to have a powerful and rapid influence in curing birds which have developed neuritis after polished rice feeding. Analogous facts, it is claimed, hold with other pyridine derivations, as, for instance, nicotinic acid. I find it somewhat hard to believe that we have here disclosed the actual nature of anti-neuritic substances as we find them in natural foodstuffs; but even if the author has made a pharmacological rather than a physiological discovery, it is none the less a remarkable one. Unfortunately, however, the first attempt to repeat the observations has failed.[40]

Owing to the initial work of McCollum and Davis,[41] belief is becoming established in the existence of two substances each of which is essential to growth; of these, one is soluble in water and the other is soluble more particularly in fats. McCollum and Kennedy,[42] feeling that the name vitamine, due to Funk, connotes

[40] A. Harden and S. S. Zilva, *Biochem. J.*, 1917, **11**, 172; *A.*, i, 612.

[41] E. V. McCollum and M. Davis, *J. Biol. Chem.*, 1915, **23**, 181, 251; *A.*, 1916, i, 184.

[42] E. V. McCollum and C. Kennedy, *J. Biol. Chem.*, 1916, **24**, 491; *A.*, 1916, ii, 451. See for the most recent contributions to this subject, *J. Biol. Chem.*, 1917, **32**, 309 and 347. The paper appeared too late for treatment in the text.

more than it should, and holding that the term "accessory food substances" as originally used by myself is too indefinite, propose to give to these two substances of unknown nature the non-committal labels "fat-soluble A" and "water-soluble B" respectively.

In connexion with this point, the practical question has arisen as to how far the various brands of margarine on the market suffer from a deficiency in the fat-soluble substance which is abundantly present in butter. W. D. Halliburton and J. C. Drummond[43] have carried out a valuable pioneer research on this subject. The curves of growth-rate presented in their paper constitute further evidence for the real existence of the factors in question. They find that the fat-soluble growth accessory is present in margarine made from beef fat and oleo oil. The vegetable oils, natural or hydrogenated, contain little or none of the substance, and margarines made from them alone are therefore, in this particular respect, inferior to butter. It is, of course, necessary to view such findings as these in proper perspective. Margarine is seldom eaten except in dietaries which contain other sources of the accessory of growth substances. The facts, nevertheless, are by no means of academic interest alone.

The question as to whether free fatty acids have a nutritive value for man and animals is of decided interest at the moment, the available supply being, for obvious reasons, exceptionally great.

Physiologists have known for half a century[44] that the animal can synthesise neutral fats from fatty acids given by the mouth, the necessary glycerol being provided by metabolism; but the limits of this capacity were not defined, and we have been uncertain as to what would be the effect of considerable quantities of free fatty acid on the intestine itself. Some feeding trials have been recently made on pigs, in which free fatty acids were made to replace two and a-half times their weight of the carbohydrate present in a control dietary. The animals receiving the fatty acids did as well as those on the control diet, but the experiments were of somewhat short duration.[45] J. F. Lyman[46] has found that palmitic acid when fed to dogs is well absorbed, showing a utilisation of more than 80 per cent. When given to cats, it was found deposited as tripalmitin.

Another point with respect to nutritional values which is of very real importance at the present time concerns the potato. Our dependence on our potato crops is likely to increase. Although

[43] *J. Physiol.*, 1917, **51**, 235; *A.*, i, 673.
[44] S. Radziejewski, *Centralbl. med. Wiss.*, 1866, No. 23.
[45] A. Lauder and T. W. Fagan, *J. Soc. Chem. Ind.*, 1917, **36**, 1069.
[46] *J. Biol. Chem.*, 1917, **32**, 7, 13; *A.*, i, 714.

nitrogenous constituents in the tuber are present in relatively small amount, it is a comfort to know that the protein has apparently an exceptionally high nutritive value, presumably because the amino-acids in it are well balanced from the point of view of animal requirements. The fact was earlier suggested by the observations of M. Hindhede[47] and of K. Thomas,[48] and it has recently received confirmation from the work of Mary S. Rose and Lenna F. Cooper.[49] They got satisfactory nitrogenous equilibrium with a daily intake of 4·8 grams of nitrogen (0·096 gram per kilo.), a result which certainly could not be obtained with a single cereal protein or with meat. It is probable that the potato will support the maintenance metabolism of the adult on, say, 0·4 gram of protein per kilo. If a reasonable amount of fat is available, the necessary calorie supply can on a potato diet be obtained with this low level of nitrogen intake.

The Growth Process; Endogenous Catalysts.

In the previous section I have dealt, more or less incidentally, with animal growth as a process affected by agents which may be classed as exogenous hormones. Growth, however, is also controlled by endogenous hormones, by agents arising within the animal itself. Whether there is any kind of relation between the exogenous and endogenous factors we do not know. The latter are contained in the internal secretions of glands, certainly in those of the thyroid, the pituitary organ, and the sexual glands. The subject of internal secretion in general does not, however, call for attention this year, but I feel that an exception should be made in the case of studies by T. B. Robertson [50] on the influence of the pituitary gland on growth.

The opinions of this author challenge attention. I devote this section to them, however, chiefly because of the experimental material on which they are based. Theories apart, this suggests that even the time relations of growth in mammals may prove to be very complex, a circumstance which must not be overlooked by other workers.

During recent years, Robertson has written many papers dealing with the general nature of the growth process.[51] His views, however speculative, doubtless call for consideration from those

[47] *Skand. Archiv Physiol.*, 1913, **30**, 97.
[48] *Arch. Physiol.*, 1909, 319.
[49] *J. Biol. Chem.*, 1917, **30**, 201 ; *A.*, i, 524.
[50] *Ibid.*, 1916, **24**, 349 ; *A.*, 1916, i, 350.
[51] For references, see *J. Biol. Chem.*, 1916, **24**, 363.

who are interested in the chemical aspects of growth; I refer to them without prejudice. They are, indeed, too complex and technical for efficient treatment here, but a few paragraphs quoted almost verbatim from the author must be given in explanation of what he considers to be the significance of the results got in pituitary feeding experiments. He believes from observation and experiment that the growth of man and of animals consists of a number of phases or growth cycles which succeed one another and to some extent merge into one another at the transitional period. Each of these cycles is characterised by an initial period of slow growth succeeded by a period of rapid growth, and that in turn by a period of slow growth, the entire cycle forming a single S-shaped curve which is symmetrical about its centre or moment of maximum velocity.

The chemical syntheses which constitute the growth of an animal are therefore of such a nature that during the first half of any given growth cycle the velocity of synthesis is progressively increased in proportion as it has already proceeded; in other words, it is auto-catalysed or self-accelerated, and as with all auto-catalysed reactions, in the latter half of the cycle growth syntheses are retarded by the progressive accumulation and mass action of the products of synthesis. Robertson claims that the formula of autocatalysis, $\log x/A - x = K(t - t')$, accurately represents the quantitative relationships of the growth process as observed whenever accurate measurements made on a sufficient number of individuals have been available. Auto-catalysis implies the existence of catalysts, and these are supplied by the glands of internal secretion.[52] The author believes that two types of growth may be recognised, called by him respectively the auto-kinetic type, in which a growth accelerator progressively increases in amount, and the auto-static, in which accelerating factors progressively diminish. For reasons fully discussed by the author, but which cannot be given here, it is suggested that increase in the mass of the catalyst will lead to an acceleration of the latter half of an auto-static or the initial half of an auto-kinetic cycle, whilst a like increase in the catalyst will retard the latter half of an auto-kinetic or the intial half of an auto-static cycle.

The influence of the pituitary secretion was studied on white mice. As a preliminary to the study, a very perfect technique for

[52] See *loc. cit.*, p. 364. I do not pretend to understand the author's position here. If growth be an auto-catalysed process, one would suppose that the velocity would be controlled by factors arising during the process itself, and therefore taking origin, not in specialised organs, but in each growing tissue.

dealing with the animals was developed. A great number of normal growth curves were recorded, and a mass of statistics concerning variation was obtained.

The mouse displays three separate extra-uterine growth cycles. The first cycle attains its maximum velocity at some time shortly prior to seven days after birth, and culminates at fourteen days. The second attains to its maximum velocity at twenty-one to twenty-three days, and culminates soon after the twenty-eighth day. The third reaches a maximum velocity at about the sixth week, and thereafter decreases in velocity continuously but very slowly, so that growth still continues between the fiftieth and sixtieth weeks succeeding birth.

Previous observations on the results of the administration of pituitary gland have suggested that material contained in the anterior lobe retards the growth of young animals.[53] Shäfer's[54] experiments, however, gave an indication that although there was retardation at early stages, there was later on no such effect, but, if anything, acceleration. Robertson's results, based on the behaviour of a much greater number of animals, confirm this. He found that the "administration of 0·125 gram per day per animal of fresh anterior lobe tissue to mice, beginning at four weeks after birth (conclusion of the second growth cycle), leads to retardation of growth during the earlier portion of the third growth cycle, that is, between the sixth and twentieth weeks. In the latter part of the third growth cycle, however, from the twentieth to the sixtieth weeks after birth, the growth of the pituitary-fed animals is markedly accelerated, so that they not only catch up the normals, but actually, at about one year of age, come to surpass the normals in weight." Presumably, therefore, the third growth cycle in mice is, in the author's sense, 'auto-static.' The administration of the pituitary substance means an increase in the concentration of a catalyst, and its effect is, according to him, similar in character to that of other catalyses of growth.

The effects are not marked, and only because they are based on much material and because the observer has so carefully considered the effect of individual variations are the experimental results worthy of attention.

Robertson has effected a partial separation of a substance from the gland which on administration has precisely the same effect on growth as the gland substance itself. This he has called

[53] See, however, E. Goetsch, *Bull. Johns Hopkins Univ.*, 1916, 146; also with regard to invertebrates. R. Wulzen, *J. Biol. Chem.*, 1916, **25**, 625; *A.*, 1916, i, 692.

[54] *Quart. J. Exp. Physiol.*, 1912, **5**, 203.

"tethelin" (τεθγλώς, growing). It is precipitated by ether from an alcoholic extract of the gland. It is a hygroscopic substance containing phosphorus and nitrogen in the proportion of four atoms of the latter to one of the former. It gives colour reactions suggesting the presence of an iminazole group, and is said to yield *i*-inositol on acid hydrolysis. The method of preparation, however, gives small guarantee for purity. In a quite recent paper,[55] experiments intended to throw light on the effect of pituitary feeding on the earlier growth cycles of the mouse are described. The attempt was made to influence the suckling by feeding the mother with tethelin. Negative results were obtained, which may have been due to the fact that tethelin fails to enter the milk. Later, during the second cycle (second to fifth weeks), acceleration of growth occurred, followed by retardation at the beginning of the third cycle, in spite of the fact that administration ceased at the end of the fifth week. When administered hypodermically to mice, tethelin is said to exert a remarkably stimulating action on the healing processes in granulating wounds.[56]

Chemistry of Bacterial Growth.

The chemistry of bacterial activity is not abstracted as part of the subject with which this Report is formally supposed to deal. I feel, however, that it is legitimate ground for one's attention. By the chemistry of bacterial activity, I mean the study of clean reactions which substances of known constitution undergo under the influence of the organisms. This study, although it began long ago, has been neglected during the development of bacterial technology with its special aims and empirical technique. It is now awakening into marked activity, and I believe it will be of fundamental importance to general biology. Unfortunately, I can say very little about it in the present Report.

The chemistry of species—the difference in chemical constitution and in metabolism which is associated with and underlies morphological difference, always a suggestive study—can be investigated with special advantages in the unicellular organisms. All the differential diagnostic methods of bacteriology are, of course, based on the variation in the metabolism of allied species.

There is something fascinating in observations such as that made by T. Sasaki,[57] who found that when *B. proteus* acts on tyrosine, it

[55] T. B. Robertson and M. Delprat, *J. Biol. Chem.*, 1917, **31**, 567; *A.*, i, 673.

[56] *J. Amer. Med. Assoc.*, 1916, **66**, 1009.

[57] *Acta Scholae Med. Kyoto*, 1916, **1**, 103; *A.*, i, 107; also *J. Biol. Chem.*, 1917, **32**, 533.

forms *d*-hydroxyphenyl-lactic acid, whereas *B. subtilis* acting on the same substance forms *l*-hydroxyphenyl-lactic acid. Special interest attaches to the fact that the products are the same, no matter whether the parent substance be *d*- or *l*-tyrosine. This is a neat case of antipodal differences in the chemical make-up of two species belonging to the same order. One would like to know what else in metabolism is correlated with a difference of this sort and how such differences arise in evolution. It is likely that a symmetrical intermediary compound is in each case first formed from the tyrosine, and the respective optical isomerides then synthesised under the direction of asymmetrical catalysts. The symmetrical intermediary might be hydroxyphenylpyruvic acid, which is formed in the animal organism by the deamination of tyrosine, or it might be hydroxyphenylacrylic acid. H. Raistrick,[58] at least, has found that histidine, when deaminated by various bacilli of the *Coli typhosus* group, gives iminoazolyl-β-acrylic (urocanic) acid.

This is an interesting observation, as it is quite possible that biological deamination of amino-acids may always begin in this way, the resulting unsaturated acids being oxidised to hydroxy- or keto-acids by a secondary process.

As is well known, different species of bacteria under varying conditions deal with the side-chain of tyrosine (and of other aromatic amino-acids) in various ways. Deamination or decarboxylation occurs, followed by oxidations of varying intensity. The side-chain may completely disappear. An anaerobic organism has, for instance, been recently isolated by A. Berthelot[59] from the intestine which, acting on tyrosine, produces, under ordinary cultural conditions, about ten times as much phenol as the most active known phenologenic species. It gave under special conditions a yield of phenol from tyrosine equal to 80 per cent. of the theoretical.

Two new points concerning the general nutrient needs of bacteria have come to light of late. F. A. Bainbridge[60] showed that many bacteria are unable to decompose pure proteins, an observation since confirmed, and shown to be true even in the case of organisms of the putrefying type.[61] It has been further shown that, as a matter of fact, small amounts of free amino-acids are necessary for the initial growth of many, if not of all, bacteria.[62] S. W. Cole

[58] *Biochem. J.*, 1917, **11**, 71; *A.*, i, 499.
[59] *Compt. rend.*, 1917, **164**, 196; *A.*, i, 305.
[60] *J. Hygiene*, 1911, **11**, 341.
[61] J. A. Sperry and L. F. Rettger, *J. Biol. Chem.*, 1915, **20**, 455; *A.*, 1915, i, 482.
[62] Rettger, Berman, and Sturges, *J. Bacteriol. Baltimore*, 1916, **1**, 15.

and H. Onslow[63] have described a medium "tryptamine" containing free amino-acids from almost completely digested casein as a successful substitute for neutral peptone media. Organisms which are naturally saprophytic, or which may have been made saprophytic by laboratory sub-culture, apparently make less demands on the specificity of the medium than do those which are more strictly parasitic. The latter are adjusted to live in the complex media represented by living tissues, and apparently need for their development special stimulating factors. It has long been recognised that blood or tissue extracts must be added to artificial media if such organisms are to be successfully grown. The work of Dorothy J. Lloyd[64] on the *meningococcus* seems to make it clear that the growth of this organism calls, as a matter of fact, for vitamines. S. W. Cole and D. J. Lloyd[65] find that the facts are the same in the case of the *gonococcus*. It is noteworthy that the metabolism of bacteria should resemble that of animal cells in dealing primarily with amino-acids, and that certain micro-organisms, at any rate, should be dependent upon growth stimulants.

These considerations lead me to refer to a somewhat remarkable series of papers by M. Jacoby. It was found that certain bacteria discovered by U. Friedemann in plant tumours were capable of decomposing urea.[66] An urease can be isolated from the organism, although imperfectly. During the progress of researches with these bacteria the author recognised that in the urease was to be found an easily detectable endocellular agent offering, in a sense, analogies to toxins and the like. He therefore set himself the legitimate and happily conceived task of studying the various nutritive conditions which might make for or against the production of the agent in the cell. On Uschinski's medium, which contains glycerol, ammonium lactate, sodium aspartate, and inorganic salts, the bacteria remain alive and capable of reproduction; but growth is poor and urease production is small. The addition of serum or of an alcoholic (not an ethereal) extract of serum[67] immediately stimulates both processes, and so does the presence of mere traces of bouillon.[68]

Up to this point we seem to have before us an instance of the necessity for a vitamine-like factor. It was found, however, that dextrose[69] in small amounts greatly stimulates the formation of urease, and the author became of the opinion that the production of

[63] *Lancet*, 1916, **11**, 1011.
[64] *J. Path. Bact.*, 1916–17, **21**, 113.
[65] *Ibid.*, 1917, **21**, 267.
[66] *Biochem. Zeitsch.*, 1916, **74**, 109; *A.*, 1916, i, 529.
[67] *Ibid.*, 1916, **77**, 402; *A.*, i, 106.
[68] *Ibid.*, 1917, **80**, 359; *A.*, i, 430.
[69] *Ibid.*, **77**, 405; *A.*, i., 106.

ferment is increased by the sugar, not merely indirectly, by stimulation of general metabolism, but because an actual precursor, in a chemical sense, of the urease is supplied. He believes that such studies will ultimately throw light on the actual chemical nature of the ferment. It became important, therefore, to define more closely the nature of substances capable of producing urease. Greatly efficient is *d*-galactose; efficient to a less degree are *d*- and *l*-arabinose, rhamnose, *d*-mannose, and many other substances tested prove ineffective. It is possible to note a common configuration in the effective sugars.[70] The 3-carbon derivatives of dextrose, namely, glyceraldehyde, dihydroxyacetone, pyruvic acid, and lactic acid, are very effective. Certain (but not all) amino-acids induce greater urease production when added to a medium already reinforced by dextrose and bouillon. From the results of the latest experiments it is claimed that good production can be obtained in the presence of simple substances only, without vitamines, that is, in Uschinski's medium with the addition of the special carbohydrates or their derivatives and certain amino-acids, for instance, leucine and *iso*-leucine.

At this stage, the remarkable observation was made that synthetic leucine could not take the place of natural leucine in promoting growth or ferment-formation. The author leaves this fact without clear explanation. If the natural leucine was made by crystallisation after pancreatic or other fermentive proteolysis, or if, as is likely, they were separated from molasses, an explanation is, I think, forthcoming; otherwise one sees none. The author's earlier experiments show how extremely small an amount of bouillon is effective in promoting growth. Only so much, for example, as is introduced when organisms from a bouillon-containing medium are subcultured into one which is bouillon-free. Now the medium in the latest experiment was intentionally made to contain no bouillon or blood, that is, no vitamine supply. I will here venture to mention an experience of my own. There had remained in my laboratory for ten years a specimen of tyrosine prepared from an autolysed pancreas. In the course of certain experiments, the aim of which I need not go into, it was found that the specimen contained the tissue kinase which coagulates blood plasma. A few milligrams added to 5 c.c. of stable fowl's plasma induce coagulation in fifteen minutes; after the tyrosine had been thrice recrystallised from water it induced coagulation in thirty-five minutes. A specimen of tyrosine prepared by acid hydrolysis of pure casein had, as was to be expected, no coagulative effect whatever. Enzymes and other biological catalysts derived from living tissues are often associated

[70] *Biochem. Zeitsch.*, 1917, **81**, 332; *A.*, i, 528; *ibid.*, **79**, 35; *A.*, i, 305.

in this close way with apparently pure crystalline preparations. In the case of growth-promoting vitamines the effective concentration may certainly be as small as that of such an agent as thrombokinase. Without knowing their origin, one cannot, of course, say, but I think it is possible that the natural leucines in Jacoby's experiments were effective because they introduced an agent from which the synthetic product was, of course, free. At least I am glad of the opportunity of asserting that in experiments of the kind almost infinitesimal amounts of material must be reckoned with.

I have given much space to Jacoby's work because I think the ideas underlying it are suggestive. Unfortunately, it seems, however, by no means certain that the substances which promote the formation of the endocellular ferment are, as the author supposes, its actual chemical precursors, able to throw light, therefore, on its constitution. It remains possible that they promote general metabolism and stimulate the formation of the ferment only indirectly.

The Pancreas and Diabetes.

The extraordinarily voluminous literature bearing on the influence of the pancreas in carbohydrate metabolism continues to grow, although there is as yet no indication that a complete understanding of that influence is at hand. Whoever first thinks of the *experimentum crucis* which will give us clear light in this dark region will earn the gratitude of students of metabolism. A paper from the laboratory of G. Embden [71] adds something definite to our knowledge. When dextrose is perfused through the liver of a normal dog it is, in part, converted into lactic acid by a reaction which is reversible. If the animal be first depancreatised, however, its liver no longer yields lactic acid from perfused sugar, but acetoacetic acid instead. Here is something very tangible, but, as is usual in this domain, it is by no means easy to correlate the new facts with the old. G. Winfield and I,[72] in experiments which have not yet been fully described, found that pancreas extracts inhibit the formation of lactic acid in muscle, and we regarded the result as further evidence to show that the pancreatic factor stabilises carbohydrate. There is perhaps no actual contradiction in these two results, but correlation is difficult. J. R. Murlin [73] having found that when alkalis are introduced directly into the duodenum of diabetics there is diminution of the glycosuria and hyperglycæmia, and finding, further, that if in the dog the pylorus is tied or the

[71] G. Embden and S. Isaac, *Zeitsch. physiol. Chem.*, 1917, **99**, 297; *A.*, i, 496.

[72] *Proc. Physiol. Soc.*, 1915; *J. Physiol.*, **50**, V.

[73] J. R. Murlin and J. E. Sweet, *J. Biol. Chem.*, 1916, **28**, 261; *A.*, i, 104.

stomach excised before pancreatectomy, the glycosuria which usually follows the operation is prevented or lessened, decides that when the pancreatic operation is performed alone it is the acid of the gastric juice, unneutralised in the absence of the gland, which poisons the liver and leads to glycosuria. I cannot think that these observations help towards an understanding of clinical diabetes.

Guanidine and Tetany.

As one of the results of an important research [74] into the physiology of the parathyroid glands carried out in the laboratories of Glasgow University, we are presented with a striking case of a circulating metabolite of known constitution bearing responsibility for the control of a normal function, and, when abnormally increased, for the production of pathological symptoms. D. Noël Paton and L. Findlay, whilst studying the condition of *Tetania parathyeopriva*, found that present views concerning the immediate cause of the tetany are unsatisfactory, and were led by certain suggestions in their work and others in the literature to consider the possibility that guanidine might be responsible for the familiar picture of the condition. They found on experiment that the symptoms of guanidine poisoning closely resemble those produced by removal of the parathyroids. D. Burns and J. E. Sharpe determined, by a process (satisfactorily controlled) which finished by the weighing of the bases as gold salts, the guanidine and methylguanidine in the blood and urine of normal and parathyrectomised dogs, and in the urine of children suffering from idiopathic tetany. The amounts found in the pathological conditions were from five-fold to eight-fold normal. It was further found that there was close similarity in the metabolic disturbances produced respectively by removal of the glands and by the administration of a salt of guanidine. The conclusion drawn from these researches is that the parathyroids regulate the metabolism of guanidine, and thus indirectly control the tone of the muscles.

Formation of Pigment in the Skin.

The chemical mechanism by which pigment is produced in the skin has always been a subject of curiosity, because of the great biological significance of epidermal coloration. On the discovery of the oxydases which produce black or coloured products from aromatic amino-acids, attention was naturally directed to them in this connexion. Tyrosinases, which certainly play a part in the

[74] *Quart. J. exp. Physiol.*, 1917, **10**, 175.

production of some animal melanins have been credited with responsibility for producing skin pigmentation, but the evidence for this has never been strong. Tyrosine itself has not offered quite satisfactory evidence of being concerned in the process. B. Bloch[75] has recently found that 3 : 4-dihydroxyphenylalanine is undoubtedly acted on by a specific oxydase actually present in human and other skins, oxidation and condensation leading under its influence to the formation of a black pigment. The evidence to show that this is really a physiological phenomenon occurring during life seems to me strong. The precursor itself has not been found in animal tissues or in the products of protein hydrolysis, but was isolated from the juice of *Vicia Faba* by Guggenheim. It is possible, of course, that it is formed in the animal body from tyrosine elsewhere than in the skin. The substance is endowed by Bloch with the uneuphonious 'portmanteau' name "dopa," and we are to speak of "dopaoxydase" and "dopamelanin."

F. Gowland Hopkins.

[75] *Zeitsch. physiol. Chem.*, 1917, **100**, 226; *A.*, i, 675.

AGRICULTURAL CHEMISTRY AND VEGETABLE PHYSIOLOGY.

The special circumstance that most countries where agricultural science is studied are now absorbed in war gives a somewhat artificial air to many of the published papers. The War has revealed weak places in our agricultural systems and research programmes, which the more strenuous of the investigators are engaged in strengthening, and in the process they are overhauling their stock of ideas and evolving better and more living programmes for future work. It could scarcely be expected, however, that the weak places should be announced, and whatever information can be gleaned from what is stated or omitted in papers published elsewhere is better utilised in other ways. In general, the published work has dealt with old problems, some of which are obviously being rounded off and got out of the way to make room for other and more important work that is not revealed. It seems inevitable, however, that agricultural science will benefit. The close co-operation now existing between the farm and the laboratory can scarcely fail to let in a flood of new ideas, facts inconsistent with old hypotheses, and new problems demanding solution, which will put out of the running many of the stock problems of the past, some of which were sadly out of touch with reality. This War is a great destroyer of artificiality, and is giving us an opportunity of revising our ideas and gaining a truer perspective than we had in the more easy-going days of the past.

Soil Chemistry.

The soil is made up of three components: mineral matter, organic matter, and soil moisture. The mineral matter is derived from the original rock; the particles have been broken up and decomposed until they are reduced to dimensions varying from 1 mm. in diameter downward, larger particles being regarded as gravel or small stones. Intimately mixed with these are residues of plants and animals in all stages of decomposition, and the whole is kept

moist by the soil water. The larger mineral particles can be studied by petrographic methods. It has been shown[1] that calcium is most commonly present in the coarser materials, such as hornblende, plagioclase, and epidote, with traces of other minerals. It does not appear, however, that the minerals recognised in the coarser particles are particularly active in the soil. Thus, neither orthoclase nor pegmatite appears to react with lime,[2] with the liberation of potash, as might have been expected. These coarser particles seem to be more important from the physical than from the chemical point of view.

Unfortunately, petrographic methods cannot be applied to the finer particles, the silts and the clay fraction, which contain by far the greater proportion of the reactive mineral matter of the soil, and no simple method has yet been devised to deal with these. Some information can be obtained by studying their reactions with other substances. So far as the more important fertilising substances are concerned, the interactions have already been shown[3] to resemble adsorptions rather than double decompositions, and more recent work[4] with a number of salt solutions of varying concentration shows that the ordinary adsorption equation holds very generally.

In working out the details of the adsorption, it is found advantageous to use a dye, such as methylene-blue, instead of a salt as the adsorbed material; the phenomena are similar and the observations can be made much more rapidly. No relationship has yet been traced between the amount of adsorption and the amount of colloidal material in the soil,[5] nor is any simple method yet known for estimating the total amount of colloidal material, although some interesting results are promised from the physical side.[6]

It is of considerable importance in soil management to be able to dislodge the adsorbed potassium from its loose combination so that it may become available as a plant nutrient, and a list has been drawn up showing the order of effectiveness of the various salts in this respect; ammonium chloride and calcium sulphate have been found to be considerably more effective than calcium carbonate.

[1] E. C. Shorey, W. H. Fry, and W. Hazen, *J. Agric. Research*, 1917, **8**, 57.

[2] L. J. Briggs and J. F. Breazeale, *ibid.*, 21; *A.*, i, 511.

[3] And again confirmed by K. Miyake, *Soil Sci.*, 1916, **3**, 583; *A.*, i, 247. who has studied the effect of various cations.

[4] J. E. Harris, *J. Physical Chem.*, 1917, **23**, 454; *A.*, ii, 443.

[5] W. Graf zu Leiningen, *Kolloid-Zeitsch.*, 1916, **19**, 165; *A.*, ii, 112.

[6] H. A. Tempany, *J. Agric. Sci.*, 1917, **8**, 312. This paper deals particularly with the shrinkage of soils.

The inorganic phosphorus compounds of the soil have received some attention. It is argued[7] that hydroxyapatite,

$$(Ca_3P_2O_8)_3Ca(OH_2),$$

is the only calcium phosphate likely to exist in the soil, since it alone is stable over the whole range of alkalinity and acidity known to occur in most soils.

A considerable part of the soil phosphorus is in organic combination, and only becomes available for the plant when the organic matter is decomposed. Thus it was found that some of the soils of Brittany responding markedly to phosphates were almost equally benefited by lime. Investigations showed[8] that only little mineral phosphate was present, but after appropriate treatment with lime, the amount became nearly doubled.

The liquid phase of the system, commonly spoken of as the soil solution, is of great practical importance, because it is the medium from which plants draw many of their elements of nutrition, and it has formed the subject of a great deal of discussion. It is by no means easy to remove it from the soil for experimental purposes, because the soil possesses marked colloidal properties and great powers of adsorbing substances from solutions. A centrifugal method of extraction has been used, but it is troublesome in application. Displacement methods would be easier if one could be certain that the adsorption relationships were not thereby being upset; paraffin oil is said[9] to be unobjectionable and effective, yielding a soil solution that contained 0·07 to 0·13 per cent. of total solids, which was thus more concentrated than ordinary drainage water. The proportions of nitrogen, potassium, calcium, magnesium, and phosphorus were found to vary in the extracts obtained from various soils, and not to be constant, as had been anticipated on Whitney and Cameron's older view.

A pressure method of extraction has also proved effective, especially for soils containing much clay or humus. In Ramann's laboratory, 3 kilos. of soil were subjected to a pressure of 300 kilos. per sq. cm. The amounts of calcium and of potassium were found to vary considerably in different extracts obtained from the surface soil, the proportions relative to the other constituents increasing as the solution became concentrated by dry weather and falling as the solution became diluted by rain. In extracts prepared from the subsoil, on the other hand, the amount of calcium showed less variation, except only for a rise at midsummer. There was evidence of a transportation of calcium and potassium from the subsoil to

[7] H. Bassett, jun., *T.*, 1917, **111**, 620; *A.*, ii, 413.
[8] C. Vincent, *Compt. rend.*, 1917, **164**, 409.
[9] J. F. Morgan, *Soil Sci.*, 1917, **3**, 531.

the surface during a prolonged period of drought. No indication was obtained, however, that soil adsorptions exercised any regulating effect on the concentration of the soil solution; an exchange of bases took place only when the proportions between the dissolved substances were altered.[10] The pressure method has also been adopted in van Zyl's laboratory, and here again the concentration of the solution varied according to manurial treatment and the season of the year; it is claimed, however, that the percentage composition of the ash remained constant.[11] A long, theoretical paper on the subject has also appeared[12] pointing out the effects of the displacement of equilibrium by the action of climate, plant roots, etc.

Some of the reactions of the soil solution are very important. In certain circumstances, iron is dissolved in the upper layer of the soil and precipitated a little lower down, forming an impermeable layer or "pan" through which water will not pass. Formerly, this was considered to be an alternate oxidation and reduction, and the possibility of bacterial oxidation still remains.[13] The action is now, however, generally regarded as a coagulation. This view has recently been critically discussed, and a study has been made of the effects of composition of soil, of climate, and of vegetation.[14]

Another and most important property of the soil solution is its reaction, whether acid, neutral, or alkaline. Plants will only tolerate a limited range of variation, and some are much more susceptible than others. Periodical additions of lime or of calcium carbonate are needed in order that a proper reaction may be maintained. Hitherto, the acidity has been expressed in terms of the amount of alkali or of lime necessary to effect neutralisation. If we knew the nature of the soil acids this would suffice, but we do not; the most diverse views are held, some regarding them as organic acids, some as iron and aluminium salts, whilst others deny the existence of acids and regard the phenomena as colloidal manifestations. The present methods do not allow of sharp discrimination between these conflicting ideas, and indeed it is possible that all three cases, and others as well, occur in nature. Evidence has been adduced to show that a clear distinction must be made between the base-absorbing power and the absolute acidity of the

[10] G. Ramann, S. März, and H. Bauer, *Int. Mit. Bodenkunde*, 1916, **6**, 27; *A.*, i, 311.
[11] J. P. van Zyl, *J. Landw.*, 1916, **64**, 201; *A.*, i, 439.
[12] O. Nolte, *ibid.*, 1917, **65**, 1; *A.*, i, 621.
[13] P. E. Brown and G. E. Corson, *Soil Sci.*, 1916, **2**, 549; *A.*, i, 248.
[14] H. Stremme, *Kolloid-Zeitsch.*, 1917, **20**, 161; *A.*, i, 512.

soil.[15] A new method is therefore needed. Several attempts have been made to see if the hydrogen-ion concentration will give useful information, and it seems quite promising. The drawback of the titration method is that it indicates only the amount and not the nature of the acid present; it does not, for example, show whether the acid is vigorous or only feeble in nature. The hydrogen-ion concentration does give this information. Sörensen showed some years ago that measurements of the hydrogen-ion concentration were of considerable value in dairy investigations, and cleared up difficulties which appeared insoluble on the older methods. Attempts are now being made to apply the method to the study of the soil. So far, only details of technique have received much attention; it is found[16] that electrometric and colorimetric methods give substantially the same results. The exponents (on the scheme suggested by Sörensen[17]) vary in the soils so far examined from 4·4 to 8·6. As an instance of the possible use of the method, two soil types in North Maine have been studied.[18] Both are extensively cropped with potatoes; on one (Washburn loam) the potato scab is common, on the other (Caribou loam) the scab is rare. In the former case the exponent is 5·2, in the latter it is 5·9, the more intense acidity of the Washburn loam being beyond the limits of toleration for the organism-causing scab. Investigations have shown[19] that certain other micro-organisms cease to grow when the exponent is less than 5·3. It is also claimed that rose mildew only occurs within a certain limited range of soil reaction.[20]

The limits of tolerance of barley have been studied,[21] and the results show that the hydroxyl ion is even more toxic than the hydrogen ion; in practice, however, the hydroxyl-ion concentration is not likely to reach the toxic limit in normal soils.

The third great component of the soil complex is the organic matter. This is largely derived from plants, and its characteristic is that it is perpetually undergoing decomposition, so that all stages are present, from the original plant constituents, the starting point in the long chain of decomposition, to the final products, carbonic acid, nitrates, and water.

[15] H. R. Christensen, *Soil Sci.*, 1917, **4**, 115; *A.*, i, 684; compare also C. J. Schollenberger, *Soil Sci.*, 1917, **3**, 279; *A.*, i, 440.

[16] L. J. Gillespie, *J. Washington Acad. Sci.*, 1916, **6**, 7; *A.*, 1916, i, 303.

[17] S. P. L. Sörensen, *Biochem. Zeitsch.*, 1909, **21**, 131; *A.*, 1909, i, 861.

[18] L. J. Gillespie, and L. A. Hurst, *Soil Sci.*, 1917, **4**, 313.

[19] W. M. Clark and H. A. Lubs, *J. Bact.*, 1917, **2**, 1. Other measurements are recorded by O. M. Gruzit, *Soil Sci.*, 1917, **3**, 289; *A.*, i, 430.

[20] A. Stutzer, *Biochem. Zeitsch.*, 1917, **80**, 143; *A.*, i., 439.

[21] D. R. Hoagland, *Soil Sci.*, 1917, **3**, 547; *A.*, i, 619.

The general method of investigation is to study the decomposition of plant constituents in the laboratory, and then to see whether the same products occur in the soil; if they are present in quantity, it is assumed that the process in the soil has been identical with that in the laboratory. Most of this work has been done in the United States, very little having been achieved in this country. Two main groups of compounds have been studied, the proteins and the carbohydrates. Perhaps the most striking product, and certainly the one that for long claimed most attention, is humus, a black, rather indefinite substance, soluble in dilute alkalis, but largely precipitated on addition of acids. A similar-looking substance has been prepared in the laboratory by the interaction of reducing sugars and amino-acids,[22] and attempts have been made to establish the identity of this artificial black substance with soil humus; proof of the identity would represent a great advance in soil chemistry. In other investigations,[23] sucrose or some other polysaccharide occurring in plants is heated or treated with acids, and the product is studied in the hope that some light will thereby be thrown on the formation of humus in the soil; the information obtained does not always, however, necessarily bear directly on the soil problem. Recently, doubts have been expressed whether the soluble part of the humus really is as important a soil constituent as the older chemists thought. Weir showed[24] in 1915 that soil from which soluble humus had been largely removed by alkalis was as productive as the original soil. The experiment is not entirely convincing, because of the possibility that other changes brought about by the treatment might obscure the effect, but at any rate it throws doubt on the traditional view that soluble humus is indispensable to soil fertility. It is urged in favour of this view that soils which are made productive by the addition of organic manures contain quantities of humus proportional to the growth of the crop,[25] but the experiment really only proves that the quantities of humus are proportional to the added manure. A sounder method has been followed by Gortner,[26] who shows that fresh vegetable matter yields to alkalis an extract which is very similar to that yielded by soil, except that it is colourless, and further, that the amount of humus is greatest immediately after the manure is added and before the supposed humifying organisms

[22] L. C. Maillard, *Ann. Chim.*, 1917, [ix], **7**, 113; *A.*, i, 251.

[23] Miss M. Cunningham and C. Dorée, *T.*, 1917, **111**, 589; *A.*, i, 513. A. Troussov, *Selskoie Khoziaistvo i Lesovodstvo. Petrograd*, 1914, **74**, 233; *A.*, i, 189.

[24] W. Weir, *J. Agric. Sci.*, 1915, **7**, 246.

[25] R. H. Carr, *Soil Sci.*, 1917, **4**, 515.

[26] R. A. Gortner, *ibid.*, 1916, **2**, 395, 539; 1917, **3**, 1; *A.*, i, 248, 311.

have begun to work. It is therefore argued that the soluble humus is not a soil product at all; the black pigment only is the result of soil decompositions, but this forms not more than 30 to 40 per cent. of the soluble humus, it contains only a relatively small proportion of the soil nitrogen, and is of no great importance in the problem of soil fertility. In this investigation, also, no evidence could be obtained that the phosphorus compounds in the alkaline extract were of more value to plants than those extracted by acids, as had been assumed by Grandeau and taught by his school.

Turning now to the second great group of plant products, the proteins in the plant break down in the soil with the formation of ammonia, which oxidises to nitrites and finally to nitrate. The first stage in the process is supposed to be the ordinary protein degradation studied in the laboratory. The van Slyke method of protein analysis has been applied to a number of soils [27] of various types, and the results show that the distribution of the nitrogen among the various fractions is substantially the same in all the soils examined. It is assumed, therefore, that the same organic compounds of nitrogen occur widely in different soil types. It is not possible to compare the figures with those directly obtained in the laboratory hydrolysis of protein, because the presence of the soil mineral matter somewhat affects the result.

Besides these attempts to group the soil constituents, efforts have been made, also largely in the United States, to isolate and identify individual compounds present. The number of possibilities is considerable, and the labour involved is correspondingly great, but a good deal of success has been achieved. This year two new constituents have been isolated, namely, cyanuric acid [28] and α-crotonic acid; [29] the latter possibly arises from cellulose through the intermediary of the β-hydroxy-acids, or else from allyl cyanide, which is present in the ethereal oils of certain plants.

In addition to this descriptive work, attempts have been made to trace out the mechanism of the change. Micro-organisms appear to be the active agents, and a vast amount of work has been done to elucidate their relationships to one another and to soil fertility. A great cycle of changes has been recognised; in the up grade, the living plant takes up the nitrates and other simple salts from the soil and elaborates them into complex organic substances rich in energy derived from sunlight; in the down grade, the organisms in the soil decompose the dead leaves, stems, etc., of the plants, pro-

[27] C. A. Morrow and R. A. Gortner, *Soil Sci.*, 1917, **3**, 297; *A.*, i, 512.

[28] L. E. Wise and E. H. Walters, *J. Agric. Research*, 1917, **10**, 85; *A.*, i, 622.

[29] E. H. Walters and L. E. Wise, *ibid.*, 1916, **6**, 1043; *A.*, i, 376.

ducing again the simpler salts out of which the plant had built up its substance, and liberating in the process the energy stored up by the plant during its lifetime, which energy serves for the needs of the soil population. In an extended series of observations on the Rothamsted plots, the curves showing the rate of production of carbon dioxide and of nitrate sufficiently resemble the curves for the bacterial numbers as revealed by counts on gelatin plates to justify the view that a causal relationship exists between these quantities.[30] The curve for nitrate accumulation, however, always lagged two or three weeks behind that for bacterial numbers, thus indicating that the formation of nitrate is dependent on some previous change, which in turn is dependent on the bacterial numbers. An obvious possibility is that the first change is the production of ammonia, which goes on simultaneously with the increase in bacterial numbers, and that this is followed by the production of nitrate, which is independent of the organisms counted on the gelatin plates; the lag then would represent the time required for the conversion of ammonia into nitrate. This is not a sufficient explanation, however, because it is known[31] that the amount of ammonia in the soil is normally at a minimum, and therefore that the rate of conversion of ammonia into nitrate must equal or be greater than that of the production of ammonia. If we are to regard the curves as related, the dividing up of the reactions must go further back, and the formation of ammonia must be supposed to involve two stages, the first being brought about by bacteria capable of growing on gelatin plates, and therefore fluctuating according to the numbers there recorded, whilst the second is subsequently and more slowly brought about by the organisms, or in another way. This delay in the production of ammonia has also been observed in studies on protein bacteriolysis.[32] It has been argued[33] that the rate of the production of ammonia can be expressed by the usual equation for autocatalysis, namely, $\log x/A - x = K(t - t_1)$, where x = amount of ammonia produced at time t, A = total ammonia produced during the process, and t_1 = time in which half the total ammonia is produced; if this observation should turn out to be well founded, it would throw important light on the whole process.

Another observation that may have an important bearing on

[30] E. J. Russell and A. Appleyard, *J. Agric. Sci.*, 1917, **8**, 385.

[31] E. J. Russell, *ibid.*, 1910, **3**, 233; confirmed by P. L. Gainey, *Soil Sci.*, 1917, **3**, 399; *A.*, i, 529.

[32] R. H. Robinson and H. V. Tartar, *J. Biol. Chem.*, 1917, **30**, 135; *A.*, i, 498.

[33] K. Miyake, *Soil Sci.*, 1917, **4**, 321; *A.*, i, 718.

the subject is that soil organisms appear by preference to attack carbohydrates, and so long as they can get these they make very little effort to break down proteins and release ammonia.[34]

It must not be assumed that bacteria are the only organisms concerned in the decomposition processes. Evidence is accumulating that there is a characteristic fungal flora in the soil which also plays a part in the reactions.[35]

The circumstance that semi-arid soils form a large area in the United States has led investigators to consider whether the soluble salts occurring in these soils cause any fundamental modification in the bacterial decompositions taking place there. No fundamental difference has been observed, although there are indications of certain differences. For example, in the case of humid soils, the rate at which ammonia is produced from organic substances, such as dried blood, mixed with the soil often gives a useful indication of the fertilising values. In arid soils, however, the rate at which nitrate is produced is considered to give a better indication.[36] If this should turn out to be correct, it would indicate that nitrifying bacteria are affected by the soil conditions in much the same way as the higher plants, whilst some of the ammonifying organisms are not. A certain amount of evidence in this direction has been adduced.[37] The effect of irrigation has been studied in some detail, and data have been accumulated; it was found[38] under the conditions obtaining at Utah that the growth of a crop caused an increase in the number of the organisms (presumably because of the crop residues thereby added to the soil), and that watering the fallow soil also caused an increase, whilst watering the cropped soil did not. It is possible that the failure of the bacteria to increase in numbers is brought about by some other limiting factor, which begins to operate when the numbers reach the 6 or 7 millions per gram attained in these experiments.

More important, however, than the watering is the effect of the soluble salts usually present in some arid soils. The effect is complex and variable.[39] Broadly speaking, the acid radicle is found[40] to play the more important part in controlling the rate of production of ammonia, the order of decreasing toxicity being usually: chlorides, nitrates, sulphates, carbonates. The phenomena closely

[34] S. A. Waksman, *J. Amer. Chem. Soc.*, 1917, **39**, 1503; *A.*, i, 613.
[35] S. A. Waksman, *Soil Sci.*, 1917, **3**, 565.
[36] C. B. Lipman and P. S. Burgess, *ibid.*, **3**, 63; *A.*, i, 243.
[37] P. E. Brown and E. B. Hitchcock, *ibid.*, **4**, 207; *A.*, i, 717.
[38] J. J. Greaves, R. Stewart, and C. T. Hirst, *J. Agric. Research*, 1917, **9**, 293.
[39] W. P. Kelley, *J. Agric. Research*, 1916, **7**, 417; *A.*, i, 431.
[40] J. J. Greaves, *Soil Sci.*, 1916, **2**, 443; *A.*, i, 243.

resemble those shown by plants; in each case, similar quantities of the various salts cause similar reductions in growth, and in each case, also, the toxicity of certain salts is readily counteracted by the addition of sufficient calcium salt.[41] Whilst the increased osmotic pressure exerted by the added salts is no doubt an important factor, it is probably not the only one in retarding bacterial activity in the soil.

It was shown some years ago that the organisms decomposing the plant residues, with the production of ammonia and nitrate, cannot be regarded as the sole inhabitants of the soil; there exists another group, including the soil amœbæ and possibly other forms, which on the whole are detrimental, but are more readily killed; hence partial sterilisation of the soil increases the rate of the production of nitrate, and therefore the fertility of the soil. Since this view was first published[42] in 1909, there has been a considerable volume of research on the subject, which has recently been conveniently summarised;[43] well above 300 papers are discussed.

It has been supposed that some physical effect is brought about during the partial sterilisation, but it is not clear that this would play any great part in the matter, because the increased fertility is no more when the soil is extracted with the antiseptic (for example, toluene) than when the two are simply brought into contact.[44]

Simultaneously with the laboratory investigations, attempts are being made to apply the results in practice, in this country in glasshouse culture[45] and in France in outdoor nursery work. Toluene, carbon disulphide, and bleaching powder are all effective agents;[46] an emulsion of carbon disulphide is proving very satisfactory at the National Reconstruction Nurseries at Versailles.[47]

No review of chemical and biochemical investigations of the soil would be complete without some reference to the work on soil physics. The problem attracting most attention is the relationship between the solid and the liquid components of the soil, especially the distribution of the liquid between the soil and the plant. Freezing-point determinations have indicated a connexion between the concentration of the soil solution and that of the root sap, which becomes especially marked at a certain low

[41] G. P. Koch, *J. Biol. Chem.*, 1917, **31**, 411; *A.*, i, 622.
[42] E. J. Russell and H. B. Hutchinson, *J. Agric. Sci.*, 1909, **3**, 111.
[43] N. Kopeloff and D. A. Coleman, *Soil Sci.*, 1917, **3**, 197.
[44] J. P. du Buisson, *ibid.*, 353; *A.*, i, 529.
[45] E. J. Russell, *Country Life*, Dec. 8, 1917, p. 548.
[46] M. Miege, *Compt. rend.*, 1917, **164**, 362.
[47] *Country Life*, Oct. 20, 1917, p. 366.

water content of the soil.[48] Relationships are also indicated between the amount of so-called "unfree" water (the water which, according to dilatometer measurements, does not freeze at $-3°$) and the so-called wilting coefficient, or water that is not available to plants.[49] Further work has been done on the relationship between the so-called "hygroscopic coefficient," the amount of moisture absorbed by dry soil from a moist atmosphere and the water-holding capacity of the soil.[50] Numerous measurements of the movement and distribution of water in soils have also been collected and discussed.[51]

Critical examinations are much needed of these various "coefficients" that have been set up from time to time by different investigators. The permeability of the soil to water, which is no doubt a related phenomenon, is influenced by the presence of dissolved salts, and the effect is probably as much chemical as it is physical in character.[52] It is shown also that the electrical conductivity of the salts is much affected by the soil colloids.[53]

Soil Formation and Soil Surveys.

Evidence is gradually accumulating that a twofold origin must be sought for the soluble salts in alkali soils. Formerly, it was held that the whole of the salts arose by weathering, and remained *in situ* because the rain was insufficient to wash them out. Now it is considered that this action, although it may take place, is too restricted to account for all the phenomena. The alkali is supposed to arise mainly from salts pre-existing in the underlying rock and deposited originally from the inland seas and lagoons which in past geological ages occurred in the regions in question. These salts are brought to the surface by irrigation water as soon as irrigation begins, and they come into contact with other salts also carried by the water or present in the soil; various interactions then take place. These account for the salts actually found on the surface; the investigations are also suggesting methods by which the trouble can be overcome.[54] The possible effect of colloidal humus substances has also been discussed.[55]

[48] M. M. McCool and C. E. Millar, *Soil Sci.*, 1917, **3**, 113.
[49] G. J. Bouyoucos, *J. Agric. Research*, 1917, **8**, 195; *A.*, i, 510.
[50] F. J. Alway and G. R. McDole, *ibid.*, 1917, **9**, 27; *A.*, i, 509.
[51] F. S. Harris and H. W. Turpin, *ibid.*, **10**, 113; (Utah Soils), H. E. Pulling, *Soil Sci.*, 1917, **4**, 239.
[52] D. J. Hissink, *Bied. Zentr.*, 1917, **46**, 138; *A.*, i, 509.
[53] M. I. Wolkoff, *Soil Sci.*, 1917, **3**, 423; *A.*, i, 621.
[54] R. Stewart and W. Peterson, *J. Agric. Research*, 1917, **10**, 331.
[55] H. Puchner, *Kolloid-Zeitsch.*, 1917, **20**, 209; *A.*, i, 532.

Soil Surveys.—During the year, an interesting survey of the soils of North Wales has been published, and the relationships between the various soils is discussed.[56] The soils differ from those examined by Hall and Russell; in particular, their coarse fractions are much more complex in composition, containing quantities of alumina and iron oxides instead of being composed almost wholly of silica. They resemble the "Steinboden" of Ramann, and form an interesting contrast with those hitherto studied in this country. It is gratifying that an investigation into their characteristics has been undertaken; it may reasonably be expected to throw much light on many of the problems of soil formation.

Manures.

In this part of the subject much more work has probably been done than has been published. The reason for this reticence is mainly the intimate relationship between fertilisers and explosives.

The nitrogenous fertilisers naturally attract most attention. Ever since Sir William Crookes's famous address to the British Association in 1898, chemists have attempted to prepare nitrogenous fertilisers direct from atmospheric nitrogen. The problem has been solved, and enormous quantities of ammonia and of nitric acid are now being synthesised on the Continent. A sufficiently general account of some of the British experiments has been issued.[57] It may be inferred that very considerable quantities of these substances will be available as fertilisers after the War, and that agricultural practice will undergo certain modifications in consequence.

Calcium cyanamide, in particular, is likely to come into considerably extended use. As hitherto prepared, it suffers from the drawback that it is too fine a powder to be easily applied to the soil; it blows about, gets into the eyes, ears, and noses of the workmen, and is a cause of considerable friction with them. One method of overcoming the difficulty, said to be successful in Germany, is to add 15 per cent. of coal tar.[58] Another method gives a product satisfactory from the physical point of view, but not from the chemical, since it leads to a certain amount of polymerisation to dicyanodiamide. Indeed, perhaps the chief drawback to cyanamide is that it is liable in certain circumstances to change to dicyanodiamide, which has little if any fertilising action, and is even harmful in excess. It is essential for the success of

[56] G. W. Robinson, *J. Agric. Sci.*, 1917, **8**, 338.
[57] E. B. Maxted, *J. Soc. Chem. Ind.*, 1917, **36**, 777; *A.* ii, 465.
[58] Schmoeger and Lucks, *Mitt. deut. Landw. Gesell.*, 1917, No. 10, 156.

the new industry that this change should be studied very fully and that some method of reversal should be discovered. Several methods of estimating the amount of dicyanodiamide have been devised, based on the fact that cyanamide gives a precipitate with silver nitrate and ammonia, whilst dicyanodiamide does not.[59]

Investigations have also been published on the constitution of cyanamide,[60] and a reaction which yields guanidine,[61] which may help to throw light on the transformation it undergoes in the soil.

It is well known that sulphate of ammonia produces harmful effects in acid soils, but whether this results from increased acidity due to removal of ammonia or to some definite toxic effect of the salt itself is not clear. Evidence has this year been adduced to show that the latter is the cause[62] where barley is concerned; on the other hand, the results with buckwheat appeared to be different.[63]

The shortage of nitrates and ammonium salts has brought into prominence other possible sources of nitrogen. First and foremost, it is essential to economise as much as possible the nitrogen compounds in the farmyard manure produced on the farm itself, which is by far the commonest and the most important of all manures. In this country, some 37 million tons of farmyard manure are produced annually, worth probably about £11,000,000; all other fertilisers consumed in the United Kingdom added together do not exceed 1·1 million tons per annum, worth about £4,540,000. It has been shown[64] that the losses of nitrogen from farmyard manure as ordinarily treated on the farm may easily amount to one-half of the total quantity, whilst the value of the lost material is still higher, because the most available compounds go first. The investigation showed that loss was due to three causes: washing out of soluble compounds by rain-water percolating through the heap, volatilisation of ammonia, and an evolution of gaseous nitrogen. This last reaction was studied in considerable detail. It was found not to go on under complete anaerobic or complete aerobic conditions; thus it is neither a simple reduction nor a simple oxidation. It requires a combination of aerobic and anaerobic conditions, such as readily occurs in an ordinary manure heap, and a general hypothesis is put forward to account for the reaction. The investiga-

[59] G. Hager and J. Kern, *Zeitsch. angew. Chem.*, 1917, **30**, I, 53; *A.*, ii, 518; A. Stutzer, *Zeitsch. angew. Chem.*, 1916, **29**, 417; *A.*, ii, 159.

[60] E. Colson, *T.*, 1917, **111**, 554; *A.*, i, 448; compare also E. A. Werner, *T.*, 1916, **109**, 1325; *A.*, i, 82.

[61] E. Schmidt, *Arch. Pharm.*, 1916, **254**, 626; *A.*, i, 449.

[62] H. G. Söderbaum, *Bied. Zentr.*, 1916, **45**, 454; *A.*, i, 192.

[63] R. C. Cook, and F. E. Allison, *Soil Sci.*, 1917, **3**, 487; *A.*, i, 623.

[64] E. J. Russell and E. H. Richards, *J. Agric. Sci*, 1917, **8**, 495.

tion brought out the fact that the ideal conditions for storage are complete absence of air and a temperature of about 26°; under these conditions no loss of nitrogen occurs, but only a breaking down of the complex nitrogen compounds with the formation of ammonia, which is entirely beneficial. These conditions are not attained on an ordinary farm, but investigations have been put in hand to devise methods for securing them.

Attempts have been made to reduce the loss of nitrogen by admixture of various substances, and it is claimed that both gypsum and sulphur are effective.[65] In a long-continued series of field trials at Ohio,[66] the addition of gypsum to farmyard manure was found to be beneficial. It is arguable, however, that the result is due to the well-known beneficial effect of gypsum in alkaline conditions.

Attempts have also been made to utilise the fermentation processes of the manure heap for increasing the solubility of the phosphate in rock phosphate. The older efforts at mixing rock phosphate with manure gave no clear indications of any increase in solubility; it is claimed,[67] however, that the further addition of sulphur does bring this about.

In order to reduce the fly pest in manure heaps, American experimenters have suggested the addition of boron compounds. Experiments have been made to ascertain whether quantities effective as a larvicide are harmful to the crop. It appears that they are not; the soluble borates, which would be injurious if they remained as such, are converted in the heap into insoluble and innocuous compounds.[68]

The liquid manure which drains away from the heap or the stables is rich both in nitrogen and in potash, and considerable attention has been paid to the proper method of storing and using it. In Germany this is regarded as one of the best ways of overcoming the shortage of nitrogen fertilisers of which agricultural writers are complaining.[69] A method said to answer well is to store the liquid in a tank under a floating wooden cover, and then to cover the whole with a thin layer of oil. This keeps out air and reduces loss of nitrogen.[70]

New sources of nitrogenous fertilisers are being exploited. The

[65] J. W. Ames and T. E. Richmond, *Soil Sci.*, 1917, **4**, 79.

[66] *Ohio Agric. Expt. Station.*, Circ. 144.

[67] P. E. Brown and H. W. Warner, *Soil Sci.*, 1917, **4**, 269. J. G. Lipman and H. C. McLean, *ibid.*, 337.

[68] F. C. Cook and J. B. Wilson, *J. Agric. Research*, 1917, **10**, 591; *A.*, i, 721.

[69] E. Blanck, *Fühlings Landw. Zeit.*, 1917, 265.

[70] C. Ortman, *Arb. Deut. Landw. Ges.*, 1916, 282.

fertilising value of city wastes is receiving attention in America, and it is shown that city refuse can be treated so as to yield both fat and a fertiliser.[71]

Efforts are also being made to obtain a fertiliser from waste leather which cannot be used otherwise. The leather is digested with sulphuric acid until it dissolves; on cooling, it sets to a glue-like substance, which can be ground to a powder. So far, the product has not commended itself to agricultural chemists in this country, but it is used in some countries as a base in compounding mixed manures; the French experiments appear to have been more successful than others.[72]

The methods of analysis of organic manures of this kind, many of which are very indefinite in composition, are naturally rather conventional; reasons have been adduced for preferring the direct nitrification test rather than the ammonification test,[73] although the alkaline permanganate method is also said to give good results.[74]

Much more interesting than these attempts to find new fertilisers (valuable although these are) are the efforts to utilise bacteria as agents in nitrogen fixation. The method is attractive, because it seems to hold out the prospect of getting something for nothing, which always appeals to frail humanity. Certain bacteria are known to absorb gaseous nitrogen and build it up into protein. This process has been carried out on the laboratory scale, and the necessary conditions are tolerably well known; there is no fundamental reason why it should not succeed on the large scale. Two types of organisms can bring it about: free living organisms such as *Azotobacter*, and organisms living in or symbiotic with leguminous plants, clover, etc. Since the reaction is endothermic, it is obviously necessary to supply a source of energy; easily oxidisable carbohydrates are found the most suitable. This, of course, limits the practical possibilities, mannitol, perhaps the most suitable source of energy for *Azotobacter*, being very costly. The pentosans, however, are found to answer, and these are more common; it has been shown[75] that horse fæces favour the fixation, but their value depends on the diet the animal is receiving, being considerably higher on a corn and hay diet than on one of grass; under favourable conditions, 4 milligrams of nitrogen are fixed for every gram of fæces oxidised. Bullock fæces also serve so long as

[71] P. J. Schroeder, *J. Ind. Eng. Chem.*, 1917, **9**, 513.

[72] R. Guillin, *Ann. Sci. Agron.*, 1916, **33**, 337.

[73] C. B. Lipman and P. S. Burgess, *Soil Sci.*, 1917, **3**, 63; *A.*, i, 243; *J. Agric. Research*, 1916, **7**, 47.

[74] C. H. Jones, *Vermont Agric. Expt. Station*, 1913, *Bull.* 173.

[75] E. H. Richards, *J. Agric. Sci.*, 1917, **8**, 299.

the animal is receiving cake, but not when he receives grass only. The investigation opens up a number of interesting possibilities.

Attempts have been made to increase the effectiveness of the clover organism by inoculating suitable strains on the seed before sowing, and this method is being recommended in Germany to help in overcoming the shortage of nitrogenous manures and proteins.[76] It appears also that inoculation of non-leguminous crops with nitrogen-fixing organisms has been attempted, although full details are not yet available.[77] Danish trials made between 1905 and 1910 have again been summarised; inoculation is shown to have been effective for the first and second years on lucerne and lupines growing on unmanured land.[78] Russian experiments have also given satisfactory results, the increase generally varying from 20 to 40 per cent.[79]

The shutting off of the supplies of Stassfurt salts has led to many efforts to obtain potassium salts from other sources. Whilst these efforts are not yet completely successful, they hold out considerable promise for the future. Blast-furnace flue dust is being used as raw material in this country,[80] and the wash-water from wool scouring has been suggested.[81] In the United States, dust from cement works,[82] kelp, and certain natural deposits of salts in some of the Western States of America[83] are being used; the total output in 1916 was equivalent to 10,000 "short" tons of potash (K_2O), this being ten times the output for 1915.[84] In the meantime, substitutes are being suggested. Sodium salts have long been known to serve, and the Rothamsted experiments have shown that both the sulphate and the chloride are effective for a period of years, although not, of course, permanently. They are being widely recommended as partial substitutes for potash even in

[76] L. Hiltner, "Vermehrte Futtergewinnung aus der heimischen Pflanzenwelt," Stuttgart, 1917.

[77] L. Hiltner, *Mitt. Deut. Landw. Ges.*, 1916, Heft 36.

[78] H. R. Christensen, *Centr. Bakt. Par.*, 1916, **46**; also in *Tidskrift f. Plantearl*, **21**, 97.

[79] I. A. Makrinov, Petrograd, 1916. An English account is given in *Bull. Agric. Intell. Rome*, 1917, **8**, 196.

[80] H. T. Cranfield, *J. Board Agric.*, 1917, **24**, 526; compare also **24**, 852.

[81] A. F. Baker, *J. Leeds Univ. Textile Assoc.*, 1915, **4**, 69.

[82] W. H. Ross, and A. R. Merz., *J. Ind. Eng. Chem.*, 1917, **9**, 1035, and numerous other papers in the same journal. From the circumstance that a new German substitute "Germaniaphosphat" (63 per cent. K_2O, 8·7 per cent. P_2O_5) is produced at the Germania Portland Cement Works at Hanover, we may perhaps infer that this kiln dust is being used in Germany also. (See *Fühlings Landw. Zeit.*, 1917, **66**, 55.)

[83] J. E. Pogue, *Smithsonian Institution Bull.*, No. 102, Part 2, 1917.

[84] *U.S. Commerce Repts.*, 1917, No. 45, p. 728.

Germany, where, contrary to expectation, the shortage of potassium salts appears to be felt.[85] Ground phonolite is being recommended in Austria as a substitute for Stassfurt salts.[86]

Gypsum is often said to increase the supplies of potash to the plant, but on wholly inadequate grounds; the Rothamsted experiments are completely against this view. American experience shows, however, that gypsum is undeniably a good fertiliser at times. It appears to act best on alkaline soils; it should never be used on an acid soil.[87] Its effectiveness appears to depend on the reaction of the soil, being determined by physiological basicity, and not by shortage of potash.

Lime is also considered to increase the supplies of potash to the plant by breaking down the complex insoluble compounds in the soil, but here there are other and more important actions as well, in particular the neutralisation of acidity in the soil and the improvement of the physical condition of the clay. Limestone also serves, but in this case much depends on the size of the particles. The finer the grinding, the greater is the activity. In practice, however, there is no advantage, and some disadvantage, in going beyond the sieves having 60 to 80 meshes to the linear inch.[88]

The action of sodium and magnesium salts on wheat has been tested in the Woburn pot-culture experiments.[89] In each case, the effect depends on the anion. Magnesium oxide had previously been shown to cause a marked increase in the nitrogen content of the grain; magnesium sulphate did not have this effect, although it caused an increase both in grain and in straw; the chloride also caused an increase at low concentrations, but proved toxic at higher concentrations. Sodium compounds behave in similar manner; the hydrate and carbonate increased the crop and also the percentage of nitrogen in the grain; the chloride gave at low concentrations an increase and at higher concentrations a decrease, whilst the sulphate gave the increase only. These results are similar to those recorded on p. 212; they differ, however, from the water-culture results obtained by Breazeale.[90]

The calcium phosphates, both natural and artificial, have continued to receive attention. It is shown[91] that tricalcium phosphate and hydroxyapatite [$(Ca_3P_2O_8)_3,Ca(OH)_2$] are the only two phos-

[85] E. Blanck, *Fühlings Landw. Zeit.*, 1916, **65**, 441; *A.*, i, 624.
[86] J. Stoklasa, *Oesterreich. Zeitsch. Zuckerind*, 1916, **45**, 421.
[87] O. Nolte, *J. Landw.*, 1917, **65**, 67; *A.*, i, 624.
[88] N. Kopeloff, *Soil Sci.*, 1917, **4**, 19.
[89] J. A. Voelcker, *J. Roy. Agric. Soc.*, 1917, **77**, 251.
[90] J. F. Breazeale, *J. Agric. Research*, 1916, **7**, 407; compare also F. B. Headley, E. W. Curtis, and C. S. Schofield, *ibid.*, 1916, **6**, 857.
[91] H. Bassett, jun., *T.*, 1917, **111**, 620; *A.*, ii, 413.

phates which can exist in stable equilibrium with an aqueous solution at 25°, and probably at other temperatures also. It is further suggested that bone phosphate is a mixture of hydroxyapatite and calcium carbonate with small quantities of adsorbed hydrogen carbonates of sodium, potassium, and magnesium. The mineral phosphates have also been discussed and a series of constitutions suggested, based on the proportions of calcium and phosphorus in successive extracts and also on the changes observed on heating the phosphate.[92] Artificially prepared phosphates have been examined and their solubility in citric acid demonstrated.[93]

Plant Growth.

It is well known that germination goes on best in pure water; dissolved substances usually cause a retardation, and at higher concentrations inhibit germination. The limiting concentrations of non-toxic salts which just prevent germination show an interesting relationship. When expressed in gram-molecules per litre, they were, for sucrose, sodium chloride, and potassium ferrocyanide, as 1 : 2 : 5, these numbers being also proportional to the number of ions formed by dissociation.[94]

After germination, the seedling usually has a sufficient supply of nutrient from the reserves stored in the seed to allow growth to go on for some time. Thus when peas are put into ordinary distilled water prepared in glass vessels, they will germinate and make considerable growth without further additions. If, however, the experiment is made in quartz vessels with very pure water distilled into a quartz condenser and receiver, then growth very rapidly stops, and the roots are glabrous and not hairy.[95] The view that pure water is toxic could not be sustained; it was shown that the stoppage arose from the circumstance that seedling growth is limited by the amount of calcium present. The reserves of calcium in the seed are only small, and as pure water stored in quartz vessels is free from calcium, it does not allow of further growth. Distilled water, however, dissolves out sufficient calcium from ordinary glass vessels to keep the plant going for some time.

Sodium chloride and ammonium sulphate produced much smaller effects, which were traced to the liberation of calcium from the envelopes of the grain. Curiously enough, however, excess of calcium also prevents the formation of root hairs on *Lepidium*

[92] G. S. Robertson, *J. Agric. Sci.*, 1916, **8**, 16.
[93] A. A. Ramsay, *ibid.*, 1917, **8**, 277; *A.*, ii, 413.
[94] P. Lesage, *Compt. rend.*, 1917, **164**, 639.
[95] L. Maquenne and E. Demoussy, *ibid.*, 979; **165**, 45; *A.*, i., 530

sativum (ordinary cress).[96] It is suggested that this is an intoxication effect.

The circumstance that the shortage of calcium in the seed seriously limits growth unless it is made good lends some colour to an Italian suggestion for manuring the crop by soaking the seed in solutions of the nutrient salts rather than applying these salts to the soil as manures. It is claimed that the plant has most need of the salts during the early periods of its life, and therefore that they should be supplied at the outset so that they can be absorbed at once[97] without risk of loss. It is claimed that considerable improvement in crop production is obtained thereby, but no great number of experiments has yet been made.

Plant Growth.—Few problems in connexion with the growth of plants have been more frequently investigated than the possibility of root excretions. In the earlier days, plants were supposed to be analogous to animals, and excretions from the roots were assumed as a matter of course; this view has always remained popular among practical men. Later on, when the soil was regarded as a mineral mass and the changes going on were considered to be purely chemical, it seemed natural to suppose that the root excretions should be acid and should dissolve some of the soil substances for the use of the plant. Still later, when it was recognised that the soil was the abode of vast numbers of organisms, bringing about the most varied changes, the necessity for assuming root excretions disappeared, and a more critical investigation of the evidence seemed to show that nothing more than carbonic acid was involved. As the well-known experiment on colouring of litmus paper or the corrosion of marble by plant roots is ordinarily done, the roots run considerable risk of being broken, when, of course, some of the acid sap may exude.[98] The experiment has therefore been repeated by growing plants in gelose coloured blue with tournesol. A rose colour is duly produced, showing that the medium becomes acid, and under the conditions of the experiment there is no possibility of root fracture. The action is not, however, confined to root hairs, as was formerly supposed; it extends to all the surface cells of the bark, both in the hairy and the glabrous regions; it begins directly the root is formed and continues all through the life of the plant. The author suggests, but without offering proof, that the acid is malic acid.

One of the difficulties in the way of accepting the view that plant roots excrete any quantity of acid is the circumstance that the

[96] H. Coupin, *Compt. rend.*, 1917, **164**, 641.
[97] C. Rossi, "Nuovo processo per la cultivazione dei cereali," Milan, 1917.
[98] H. Coupin, *Compt. rend.*, 1917, **165**, 564.

water or sand used as the medium tends to become alkaline after a time. It is shown[99] that plants vary in this respect; yellow lupine (*Lupinus luteus*), and to some extent buckwheat and hemp, accumulate no bases in the solution, but tend to make it acid, whilst *Camelina sativa* leaves an alkaline residue which injures the crop if it accumulates. From the narrow point of view of technique this is interesting, because it indicates that modifications of the formula for a culture solution which hinder the accumulation of bases in the solution during plant growth are likely to be beneficial. From the broader, physiological point of view the observations afford interesting evidence of the kind of interaction taking place between the plant root and the soil solution. The changes in reaction are not necessarily due to root excretions, but might be caused by selective absorption; certain ions are more needed than others, and are therefore taken up to a greater extent, whilst those left unabsorbed impart the reaction to the solution.

Selective absorption does not, however, explain another set of phenomena investigated at the Woburn Fruit Farm. Plants suffer very considerable diminution in growth when they are grown in such a way that the water supplied to them has had to come in contact with the roots of other growing crops.[1]

The effect is quite general; it is produced by all the plants examined. The water does not retain this toxic character for long, and if exposed to air the toxin is not only lost, but converted into something useful to the plant. Accepting the obvious explanation that the roots excrete a toxin, it appears to be necessary to suppose, further, that a plant is at least as much affected by its own toxins as by those produced by its neighbours. Plants grown in pots divided up into compartments, so that each individual root was kept distinct from its neighbour, made no better growth than plants grown in undivided pots, where the roots of the different plants mingled freely. Further, within certain limits as to distance apart, the weights of the plants obtained are inversely proportional to the bulk of the soil in which they grow, or, in other words, the total plant growth is the same whatever the number of plants. Pot experiments made at Rothamsted[2] show that wheat grown along with poppy, black bent, or spurry made better growth per individual plant than wheat grown alone (the total number of plants per pot being kept the same); thus, the individual wheat plant suffered less from the presence of the weeds than from an equal number of wheat plants.

[99] E. A. Gemtchoughenikov, *Reports Moscow Agric. Inst.*, 1916, **10**, 337.
[1] S. U. Pickering, *Ann. Bot.*, 1917, **31**, p. 181.
[2] Miss W. E. Brenchley, *New Phytologist*, 1917, **16**, 53.

When the amount of space per plant becomes considerable and sufficient care is taken to ensure soil aeration, very good growth becomes possible. Methods have been suggested for increasing the growth of wheat on the large scale by allowing more space per plant and repeatedly cultivating and earthing up.[3]

It is well known that plants generally take up their nitrogen in the form of nitrates from the soil; they can utilise other compounds, including ammonium salts, but they usually thrive best on nitrate. Maize, however, takes up various organic nitrogen compounds and also sulphate of ammonia, and with some of these, including sulphate of ammonia, it is said to make better growth than with sodium nitrate.[4] Ammonia absorbed in this way is supposed to be transformed into asparagine, which is then converted into protein. Some plants, barley, maize, pumpkin, etc., readily take up ammonia and effect the conversion;[5] others, such as peas and vetches, only assimilate ammonia in the presence of calcium carbonate; whilst others, such as lupine, will not take up ammonia at all, even in presence of calcium carbonate. It is suggested that this difference is due to the different quantities of carbohydrates at the disposal of the plant; by increasing or diminishing the amount of carbohydrate, it is possible to pass from one type to another. In a state of inanition, the faculty for forming asparagine is lost; with plentiful supply of carbohydrate, on the other hand, even plants of the lupine type did not suffer from ammonia, but converted it into asparagine. An interesting difference is thus brought out between plants and animals. The animal organism can protect itself economically against the bad effect of an accumulation of ammonia by excreting it as urea in which the carbon is fully oxidised, so that no calories are lost. This simple plan is not, however, open to the plant, should an accumulation of ammonia arise through derangement of the normal protein synthesis or because ammonium salts are offered direct to it. The plant cannot excrete ammonia, but, being better supplied with carbohydrate than the animal, it can afford the luxury of making asparagine, which is richer in carbon than urea. Asparagine can accumulate in the plant without detriment, and can be built up into protein when sufficient carbohydrate is present.

On the other hand, if for any reason the plant is insufficiently supplied with carbohydrate, these conditions no longer obtain; it is then worse off than the animal, because it has no mechanism whereby

[3] H. Devaux, *Compt. rend.*, 1917, **164**, 191.

[4] R. O. Brigham, *Soil Sci.*, 1917, **3**, 155; *A.*, i, 374.

[5] D. N. Prianichnikov, *Moscow Agric. Instit.*, 1916, **10**; *Bull. Agric. Intell. Rome*, 1917, **8**, 204; *A.*, i, 616.

the ammonia can be excreted; accumulation may produce disastrous effects. It is not difficult to imagine conditions in which this might happen. The common mosaic disease of tobacco, the cause of which is not yet understood, may be a case in point; as a matter of fact, ammonia has been found in tissues affected by the disease, although it is absent from healthy tissues.[6] In this case, it is suggested that the ammonia may arise from the reduction of nitrate, since nitrites were also found. Normally, this action is prevented by the oxydases, but it goes on when the plant is infected with nitrate-reducing organisms, and not only yields ammonia, which is toxic, but it also reduces the amount of nitrogen available for useful purposes in the plant.

In discussing the transformation of nitrogen compounds in the plant, it is unsafe to confine attention solely to the ammonia, amino-acids, and proteins. Another group of compounds, the cyanogenetic glucosides, is widely distributed in plants, and one must also consider the possibility that hydrogen cyanide is in some way involved in protein formation. The synthesis[7] of mandelonitrileglucoside, sambunigrin, and similar plant constituents from ethyl mandelate and ammonia is therefore of considerable interest as showing the possibilities of converting ammonia into a cyanogenetic glucoside.

The carbohydrate constituents of plants come in for a good deal of investigation. Various sugars occur in the leaves, and further determinations of their amounts have confirmed the justice of the view put forward by H. T. Brown, and supported by W. A. Davis and others, that the first product of assimilation is sucrose.[8]

The more complex carbohydrates have proved more difficult to study, and some of them are only vaguely characterised, because of their insolubility or their colloidal properties. Further studies have been made of the pectin substances, which are important constituents of the carbohydrate group. The method of extraction has been improved,[9] and evidence is adduced to show that the pectin of the cell membranes of plants is a calcium magnesium salt of a complex anhydro-arabino-galactose-methoxy-tetragalacturonic acid.[10] The pectin of wood, however, appears to be different;[11] the

[6] P. A. Boncquet, *J. Amer. Chem. Soc.*, 1916, **38**, 2572; *A.*, i, 74; P. A. Boncquet and Mary Boncquet, *ibid.*, 1917, **39**, 2088; *A.*, i, 683.

[7] E. Fischer and M. Bergmann, *Ber.*, 1917, **50**, 1047; *A.*, i, 657.

[8] W. Gast, *Zeitsch. physiol. Chem.*, 1917, **99**, 1; *A.*, i, 433.

[9] S. B. Schryver and Miss D. Haynes, *Biochem. J.*, 1916, **10**, 539; *A.*, i, 245.

[10] F. Ehrlich, *Chem. Zeit.*, 1917, **41**, 197; *A.*, i, 321.

[11] T. von Fellenberg, *Mitt. Lebensmittelunters. Hyg.*, **8**, 1; *A.*, i, 616.

problem has been studied by measuring the quantity of methyl alcohol yielded on decomposition.

From a study of their electrical properties, it has also been suggested that the pectin substances, besides acting as the binding material of plant tissues, constitute a means for regulating the content of hydrogen- and hydroxyl-ions in the circulating fluids of the tissues and maintaining the cell contents in a slightly acid condition; they form a reserve of insoluble acid which is, nevertheless, readily available for the neutralisation of any alkaline substance brought into contact with the cell.[12]

Other constituents of plants have also received attention; a new method of testing for flavones has been described, and in view of the results obtained,[13] it is suggested that these substances serve to absorb ultra-violet rays of sunlight and protect the living protoplasms from their injurious action.

The methods of detecting carotinoids have also been studied.[14] An investigation on solanine from potato shoots indicates that the formula is $C_{52}H_{91}O_{18}N$, and that on hydrolysis it yields equimolecular proportions of dextrose, galactose, rhamnose, and solanidine, to which the formula $C_{34}H_{57}O_2N$ is assigned. The development of Molisch's microchemical methods has extended the number of known plant constituents.[15]

Attention has been devoted to the variation in composition of plants with variations in the conditions of growth. It is well known that the seed is only slightly alterable in composition, and in particular that changes in manuring and in culture have only a small, and from the practical point of view almost negligible, effect. Seasonal factors are more potent, and attempts have been made to reproduce them by artificial changes in water supply. A prolonged investigation of the composition of wheat grown under dry farming and under irrigation in Idaho[16] has, however, revealed no differences between varieties grown under these very different moisture conditions. Each variety keeps its own characteristics regardless of the changes in conditions of growth. The only practicable method of altering the composition of the wheat grain appears to be to carry into one variety the properties and constituents of another, which can be done within certain limits by suitable breeding methods.

[12] S. Odén, *Int. Zeitsch. phys. chem. Biol.*, 1917, **3**, 71; *A.*, i, 436.

[13] K. Shibata, I. Nagai, and M. Kishida, *J. Biol. Chem.*, 1916, **28**, 93; *A.*, i, 107.

[14] C. van Wisselingh, *Flora*, 1917, **177**, 371; *A.*, ii, 554.

[15] H. Molisch, *Ber. Deut. bot. Ges.*, 1916, **34**, 154; 1917, **35**, 99; *A.*, i, 505, 506, 507.

[16] J. S. Jones and C. W. Colver, *Idaho Agric. Expt. Sta. Bull.*, 88, 1916.

The vegetative parts of the plant, however, are more susceptible to variation in composition, although here again the essential functioning materials of the plant may remain uniform in composition, whilst the variations in the whole plant may be due to the precipitation of substances that have been absorbed, but are not needed,[17] or to a variation in size of the storage vessels allowing greater accumulation of storage products. The classical instance is afforded by the sugar-beet. By growing seed only from the roots richest in sugar, the Germans have steadily increased the percentage of sugar in the ordinary crop. The French chemists have now obtained as good results as the Germans.[18]

These and other instances have satisfied practical men that the composition and quality of crops can be altered fairly considerably. There are, however, limits beyond which change does not go which are not always clearly recognised. Thus the orange growers of California consider that large dressings of ammonium sulphate sweeten the fruit, and that potash increases the acidity; chemical analyses do not bear out these views.[19]

One of the difficulties of the investigation is the number of varieties and sub-varieties of the different plants. In comparing one plant with another, the greatest care is necessary to ensure that the two are really comparable. Whether the botanical differences are associated with chemical differences is not yet clear; the work is so far only in the early stages. As an example, the properties of millet specially adapted to a dry climate are being studied, and although the work is as yet still in the botanical stages, it possesses considerable interest for agriculturists.[20]

Differences in composition of different varieties are, of course, only to be expected, and whilst nothing very definite has yet emerged, some few observations have been made, which, however, require careful investigation. Thus it is stated[21] that the composition of the essential oil varies according to geographical position, even with plants of the same species; the iodine number (which indicates the relative proportions of the triglycerides of oleic, linoleic, and linolenic acids respectively) increasing as the

[17] A few attempts have been made to trace the means whereby the plant disposes of non-essential materials presented to the roots and taken up by them. Saligenin appears to be transformed into salicin, quinol into glucoside. G. Ciamician and C. Ravenna, *Gazzetta*, 1917, **47**, ii, 99; *A.*, i, 681.

[18] E. Saillard, *Compt. rend.*, 1917, **165**, 508.

[19] H. D. Young, *J. Agric. Research*, 1917, **8**, 127.

[20] C. A. Bielov, *Petrograd. Bull. of Applied Botany*, 1916, **9**, 333; *Bull. Agric. Intell. Rome*, 1917, **8**, 1093.

[21] G. V. Pigulevski, *J. Russ. Phys. Chem. Soc.*, 1916, **48**, 324; *A.*, i, 189.

geographical distribution of the plant extends further to the north.

It is important for the plant that some at least of the reactions taking place in its cells should proceed rapidly, and as it can tolerate neither rise of temperature nor increased concentration of the sap beyond certain limits, the activation has to be brought about by catalysts. The enzymes of the cell are therefore extremely important. Of these, oxydases have received a good deal of attention. They are stated [22] to increase as the plant is improved by cultivation and selection. In the case of the Japanese medlar, for example, the improved variety, with its longer biological cycle and longer, larger, sweeter, and less acid fruit, is, under equal conditions, richer in oxydases than the less cultivated variety with shorter biological cycle, and fruit which is round, small, more acid, and less rich in sugar. In other cases also the amount of oxydase was found to be inversely related to the amount of acid and directly related to the quantity of sugar present. It is further suggested that the increase in the amount of oxydase in the cultivated varieties may be associated with the additional supply of nitrogen in the soil resulting from the use of additional fertilisers.

Plant Poisons.—Studies of the effect of coal gas on plants [23] have shown that gas itself is harmful at certain concentrations, but the poisonous constituent is neither carbon monoxide, ethylene, nor acetylene; it was not identified with certainty. Cress was much less sensitive than tomatoes, salvia, and other plants.[24]

Poisoning from copper is reported from a copper tailing region in the United States. Most of the flora of the district seem to have been destroyed, and among the larger shrubs only the wild rose flourished. The surviving plants contained in their tissues appreciable quantities of copper, arsenic, antimony, and tin, as much as 0·62 per cent. of copper being present [25] in some cases.

Diseased leaves of citrus trees affected by mottling have been examined, but no great amount of information has been obtained. They contained on the average more calcium, magnesium, and phosphorus than healthy leaves,[26] which seems to indicate some functional derangement, but throws no light on its nature.

[22] A. Degli, *Annali della R. Scuola Sup. di Agric. Portici*, 1917, **14**.
[23] C. Wehmer, *Ber. Deut. bot. Ges.*, 1917, **35**, 403; *A.*, i., 618.
[24] Miss S. L. Doubt, *Bot. Gaz.*, 1917, **63**, 209; *A.*, i, 619.
[25] W. G. Bateman, and L. S. Wells, *J. Amer. Chem. Soc.*, 1917, **39**, 811; *A.*, i, 373.
[26] C. A. Jensen, *J. Agric. Research*, 1917, **9**, 157, 253.

Feeding Stuffs.

Although the physiological aspects of animal nutrition are more properly discussed in another section, reference may be made here to certain agricultural applications of some of last year's work.

The War has reduced the supplies of certain hitherto widely used feeding stuffs and brought into prominence others less known in this country. Palm-nut cake is one of the most important of these, and it has formed the subject of several interesting investigations at Leeds. It is more digestible and contains more food units than undecorticated cotton-seed cake,[27] and it compares favourably in keeping qualities with other cakes.[28] Apparently its fat does not pass as such into the milk of the cow, but is subject to some selective action, the acids of lower molecular weight being transferred in greater proportion than those of higher molecular weight; further evidence is needed, however, before this can be regarded as definitely established.[29]

Other possible feeding stuffs have been examined. Dried yeast appears to be distinctly promising, and it proved as digestible as any food on the farm.[30] Horse chestnuts have been studied both in France and in Germany. The older attempts to utilise them failed, because the cost of collection was too great. Further, the shell causes a good deal of trouble; it can be removed without difficulty in the fresh state, but it adheres to the cotyledonous mass when dried. Moreover, the shell contains both æsculin and a tannin known as æsculitannic acid. The dry, cotyledonous part is valuable; it contains 20 to 30 per cent. of starch, 6 to 7 per cent. of nitrogenous matter, and 2 to 3 per cent. of fat, but no æsculin or tannin. It contains, however, a saponin, which has a marked physiological action on the blood system, and therefore it cannot be used direct for cattle feeding. This substance can be washed out with 1/1000-hydrochloric acid, and no doubt with other acids; 20 to 25 per cent. of a beautiful, white, tasteless and odourless starch, which can be extracted and used for alcohol or even food, whilst the residue can serve as cattle food.[31]

Although the German methods of treatment of horse chestnuts have not been divulged, they are evidently considered satisfactory,

[27] C. Crowther and H. E. Woodman, *J. Agric. Sci.*, 1917, **8**, 429.
[28] W. Godden, *ibid.*, 419.
[29] C. Crowther and Miss H. Woodhouse, *ibid.*, 451.
[30] C. Crowther and H. E. Woodman, *ibid.*, 448.
[31] A. Goris, *Compt. rend.*, 1917, **165**, 345; see also P. Dechambre, *Compt. rend. Acad. Agric. de France*, 1917, **3**, 926.

as no less than 150 marks per ton is paid for them.[32] Acorns are considered even more valuable, their price being 190 marks per ton. It is said that cattle food is being made in Germany from wood meal, heather meal, and certain lichens. It has been shown in this country that both acorns and horse chestnuts yield a considerable quantity of alcohol on fermentation, some 145—164 litres of absolute alcohol per ton of nuts as picked.[33]

Experiments have been made in Germany with certain new foods and substitutes—"Ceralis," "Maizena," "Körnerblutfutter," etc., the composition of which is not indicated.[34] It has been suggested in America that insects might make good food for poultry, especially as the van Slyke method shows that the protein of grasshoppers and "June bugs" is similar to that of very tender roast beef or breast of turkey.[35]

More complete studies have also been made of the ordinary feeding stuffs of the farm. The potato is being exalted as human food, Hindhedes's older demonstration of the high nutritive value of its nitrogen compounds being supported by more recent determinations.[36] Wheat, on the other hand, is shown to be an incomplete diet for animals (like most other single foods); the "deficiency" effects are seen not only in the animal, but also in its offspring.[37] Maize "deficiencies" have also been studied,[38] and the question is raised whether lysine is the limiting amino-acid in its protein. Lastly, serious attempts are being made in Germany to improve the feeding value of straw by digesting it with dilute sodium hydroxide solution.[39]

The old problem of silage fermentation has received further attention. It is now generally recognised that the changes are brought about partly by the enzymes of the plant and partly by micro-organisms. Determinations of the rates of the various changes have shown that the production of acid is expressible by peaked curves similar to those often given by bacterial actions, whilst the hydrolysis of the proteins and the evolution of carbon

[32] Borgmann, *Tharandter Forst. Jahrbuch*, 1916, **67**, 367; abs. in *Bull Agric. Intell. Rome*, 1917, **8**, 1127.

[33] J. L. Baker and H. F. E. Hulton, *Analyst*, 1917, **42**, 351.

[34] A. Richardsen, *Landw. J.*, 1916, **49**.

[35] J. S. McHargue, *J. Agric. Research*, 1917, **10**, 633.

[36] M. S. Rose and L. F. Cooper, *J. Biol. Chem.*, 1917, **30**, 201 : *A.*, i, 524.

[37] E. B. Hart, E. V. McCollum, H. Steenbock, and G. C. Humphrey, *J. Agric. Research*, 1917, **10**, 175; E. V. McCollum, N. Simmonds, and W. Pitz, *J. Biol. Chem.*, 1916, **28**, 211; *A.*, i, 184.

[38] E. V. McCollum, N. Simmonds, and W. Pitz, *J. Biol. Chem.*, 1916, **28**, 153; *A.*, i, 192; *J. Biol. Chem.*, 1917, **28**, 483, *A.*, i, 185.

[39] *Deut. Landw. Presse*, 1917, **44**, Nos. 2, 4, 8, 9, 16; *Illustr. Landw. Zeit.*, 1917, **37**, Nos. 3 and 4; and *Wiener Landw., Zeit.*, 1917, No. 5229.

dioxide are expressible by smooth curves resembling those often shown by enzymes.[40]

Mannitol is said to be one of the products of the decomposition of the sucrose, although after a few days it suffers decomposition.[41]

Milk.

The distribution of the fatty acids in the milk fat of the cow and the sheep has been determined.[42] It has been shown that the rate of increase of the growth of lambs is related to the milk yield of the ewe.[43]

Fermentation.

It has been shown by Buchner and Albert that yeast on treatment with acetone yields a white powder capable of fermenting sugars. This material, known as zymin, owes its fermenting power to two constituents (or groups of constituents), each necessary to the work of the other, known respectively as the enzyme and the co-enzyme. The latter can be washed out with water; the residual "washed zymin" is then inert towards sugar. The extract has been investigated, but the precise active agents have not been absolutely determined. Phosphates were shown by Harden and Young to be essential, but not the sole agents. When, however, potassium pyruvate is added as well as the phosphate, the power of effecting fermentation is completely restored.[44] The addition of acetaldehyde and potassium or ammonium phosphate, but not sodium phosphate, has the same effect. These observations are interesting in connexion with a hypothesis, favourably regarded by many investigators, that acetaldehyde is an intermediate product in alcoholic fermentation, being reduced to alcohol by hydrogen liberated at a previous stage of the process. The acetaldehyde is thus supposed to start the reaction by "accepting" the hydrogen. Whether or not acetaldehyde is the co-enzyme cannot, of course, be stated without more exhaustive investigation of the extract; some other reducible substance might play the same part. The investigation has, however, carried the problem a distinct stage further by proving the necessity in the co-enzyme of phosphates, potassium or ammonium ions, and acetaldehyde or some similar substance.

[40] A. R. Lamb, *J. Agric. Research*, 1917, **10**, 361; see also O. W. Hunter, *ibid.*, 75, and C. O. Swanson and E. L. Tague, *ibid.*, 275.

[41] A. W. Dox and G. P. Plaisance, *J. Amer. Chem. Soc.*, 1917, **39**, 2078; *A.*, i, 683.

[42] C. Crowther and A. Hynd, *Biochem. J.*, 1917, **11**, 139; *A.*, i, 608.

[43] E. G. Ritzman, *J. Agric. Research*, 1917, **8**, 29.

[44] A. Harden, *Biochem. J.*, 1917, **11**, 64; *A.*, i, 501.

It is well known that yeast juice contains a powerful digestive enzyme of the trypsin type, and in consequence that it steadily loses its albumin on keeping. This enzyme can also bring about the decomposition of polypeptides, but the change is complex, depending not only as to its rate, but also to some extent as to its nature on the conditions of the experiment.[45] The effect of the hydrogen- and hydroxyl-ion concentration was studied in some detail, but it was recognised that other factors came in as well, some of which were rather indefinite, such as the unexplained condition of the ferment. The enzyme is most stable with a hydrogen-ion concentration of about 3×10^{-7}. The resulting amino-acids retard further decomposition. The results indicate a similarity in action with that observed by Bredig on inorganic ferments, and they do not necessitate the view that the ferment is active only towards a definite grouping of atoms.

The nutrition of the yeast plant is of enormous practical interest nowadays, in view of the circumstance that yeast is capable of serving as food for human beings and for animals, and that it can rapidly synthesise protein from inorganic nitrogen or from carbamide. Circumstantial accounts are received from Germany of the successful production of considerable quantities of food in this way. Organic acids (citric, acetic, tartaric), glycerol, asparagine, mannitol, and carbohydrates, including in suitable circumstances the pentosans, can all serve as sources of carbon.[46] Where sugar is used, the weight of yeast can be increased considerably by the addition of suitable quantities of gum arabic, rye gum, or the humic substances of peat.[47] The effects of fractional additions of sugar, of added alkali, and of nitrogen nutrient have been studied.[48] Instead of ammonium salts, other nitrogen compounds can serve, including pyridine, piperidine tartrate, conine, nicotine, cinchonic acid, quinine, brucine, cocaine, and morphine, but these are of less practical interest.[49]

It has been suggested that the fermentation of sugar by *Aspergillus niger* is an oxidation proceeding in three stages, producing citric, oxalic, and carbonic acids respectively, and by regulating the conditions it has been found possible to check the reaction at the first stage so as to obtain a considerable yield of citric acid.[50]

E. J. Russell.

[45] E. Abderhalden and A. Fodor, *Fermentforschung*, 1916, **1**, 533; *A.*, i, 306. [46] T. Bokorny, *Münch. Med. Woch.*, 1916, **63**, 791; *A.*, i, 72.
[47] L. Lindet, *Compt. rend.*, 1917, **164**, 58; *A.*, i, 188.
[48] T. Bokorny, *Allg. Brau. Hopfen. Zeit.*, 1917, **57**, 447; *A.*, i, 681.
[49] F. Ehrlich, *Biochem. Zeitsch.*, 1917, **79**, 232; *A.*, i, 309.
[50] J. N. Currie, *J. Biol. Chem.*, 1917, **31**, 15; *A.*, i, 614.

CRYSTALLOGRAPHY AND MINERALOGY.*

The two years that have elapsed since the last Report have been marked by a great diminution of published researches, especially of those we could ill dispense with. This is only to be expected, since the energies of many workers are now directed in other channels. In such times as these, it is no easy matter either to collect the bricks or to erect those that are shapely into an orderly structure, so that a certain degree of indulgence may well be claimed of a reader. A brief estimate of general tendencies and results will serve as an introduction to the systematic discussion of details.

The *X*-ray methods of investigating molecular structure have been fundamentally extended by Debye and Scherrer,[1] who have devised a method of experimentation which is not merely applicable to a crystal-aggregate (say, a graphite pencil), but even to ordinary liquids. Unfortunately, these publications are not at present accessible for detailed study, so that a full appreciation of this remarkable advance must be postponed. It may, however, be stated that the authors have deduced the crystal structure of graphite and the molecular dimensions of the liquid benzene molecule! The former proves to be rhombohedral; the absolute dimensions of the rhombohedral cell ($a=b=c$) are $4{\cdot}48\times10^{-8}$ cm.,

* The former title of this Report ("Mineralogical Chemistry") was initially adopted on the principle that Reports should as far as possible follow the main divisions into "Abstracts." It is, however, manifestly impossible for a Reporter on "Mineralogical Chemistry" to adopt this counsel of perfection: in the first place, because the centre of gravity of mineralogical research has shifted from chemical analysis to the investigation of mineral problems from the point of view of physical chemistry; and, secondly, because the main results of crystallography are spread over the physical, inorganic, and organic abstracts. The present title is a compromise between "Mineralogical Chemistry" and "Crystallography"; it is, perhaps, satisfactory as not being altogether at variance with the subject-matter discussed—an objection which has been good-humouredly lodged against the present writer's previous Reports.

[1] P. Debye and P. Scherrer, *Nachr. Ges. Wiss. Göttingen*, 1916; *Physikal. Zeitsch.*, 1917, **18**, 291; *A.*, ii, 437; compare also S. Kyropoulos, *Zeitsch. anorg. Chem.*, 1917, **99**, 197; *A.*, ii, 468.

which gives $d_{111} = 3{\cdot}41 \times 10^{-8}$ cm., a value agreeing well with Bragg's preliminary determination.[2] The molecule of benzene fulfils most chemical expectations; its form is that of a regular hexagon, with an edge-dimension equal to $6{\cdot}02 \times 10^{-8}$ and a "thickness" of something under $1{\cdot}19 \times 10^{-8}$.

Mention may well be made here of the publication of a series of papers by Fedorov, who has made a critical study of W. H. and W. L. Bragg's results.

Apart from the above, the progress of *X*-ray investigation is of a mixed character. Our most notable *X*-ray analysts[3] have undoubtedly unravelled the intricacies of some point systems, and have thereby laid the foundations of a crystal-structure of precision; but there would seem to be signs that it would be more prudent to devote some time to the examination of two fundamental properties, namely, the falling away of reflection-intensity with increase of "order," and the quantitative relationship between reflection-intensity and atomic mass or number, than to add another reconstruction or two to the present list. After all, the future reconstructions of crystal edifices ultimately depend on these two fundamentals, and the investigation of the simplest possible isomorphous groups (especially the group rubidium chloride, bromide, and iodide) would go far to standardise these points d'appui. In any case, numerous crystalline substances have now been thoroughly investigated, and it is possible to estimate the degree of cogency of some previous beliefs; both topic-axes and the Bravais principle have received a measure of support. On the other hand, the question of the existence or non-existence of molecules in a crystal, although actively discussed, has, perhaps not unnaturally, made no headway.

The appearance of the fourth volume of Groth's "Chemische Krystallographie," dealing with monocyclic compounds, is announced.

A certain degree of interest is attached to the first example of a medical application of crystallo-chemical analysis.[4] The identification as salol (phenyl salicylate) of a crystal of intestinal origin presented no difficulties, and was, in fact, effected in sixty-five minutes.

Steady progress has been made in the examination of silicate equilibria by the American Geophysical School. To quote Bowen: "It is not long since the discussion of the theory of the crystallisation of igneous rocks was carried out by describing the crystal-

[2] W. H. and W. L. Bragg, "*X*-Rays and Crystal Structure," 174.
[3] W. H. Bragg, *T.*, 1916, **109**, 252.
[4] T. V. Barker, *Lancet*, 1917 (May 26th), 798.

lisation of some simple binary eutectic mixture, such as salt and water, and winding up with the statement that the crystallisation of the igneous rock is in some measure analogous." Our knowledge of silicate equilibria has now certainly advanced beyond that stage, for the accurate investigations of Bowen and others have reached the point from which it is possible to sketch the main outlines of petrogenesis; the painstaking field observations of generations of petrographers, leavened not merely by the principles but also by the practice of physical chemistry, are rapidly giving rise to a science of petrology.

The last topic to be discussed is crystal growth (and dissolution). The characteristic, plane-polyhedral form assumed by a growing crystal is as pleasing to behold as it is difficult to "explain." Drops of a liquid, separating in a state of suspension from another, usually assume spherical forms—bodies having the least area for a given volume. Not so crystals; although isolated examples are known partly or wholly bounded by curved surfaces, whilst others, owing to an all-round, richly faceted development, would seem to approximate towards a spherical form, it is nevertheless certain that the most frequent styles of development are the thin plate or fine needle—shapes which are extreme examples of a maximum of area for a given volume. This "anomaly" Curie attempted to reconcile with the principle of minimum surface energy by assuming that plane faces are developed because they have lower capillarity constants than curved faces. His theory has been exceedingly fruitful, for it has stimulated research in a province which otherwise might not have been explored. Recent work, however, has proved it to be untenable for macroscopic crystals. Further, it is not generally known that the problem had been previously, and more satisfactorily, handled by Gibbs in his work on the Phase Rule. Gibbs, indeed, foresaw that the principle of minimum surface energy might only operate in the case of microscopic crystals. The present appears to be a suitable time to review the problems of crystal growth, inasmuch as future work is likely to take other directions. The inverse question of crystal dissolution is even more complex, but some regularities have been noted.

General Results of X-Ray Methods of Investigation.

The most efficient form of installation for the preparation of X-radiograms has been discussed by Rinne.[5] The employment of the Lilienfeld X-ray tube is advocated as permitting a steady

[5] F. Rinne, *Ber. K. Sächs. Ges. Wiss.*, [*Math.-Phys. Klasse*], 1915, **67**, 303.

stream of rays of any desired hardness. Analysis of a radiogram is shown to be most directly and easily effected by the help of a gnomonic projection, from which the stereographic projection can be readily obtained. Great care must be employed when adjusting the crystal, otherwise a want of symmetry may appear in the radiogram (it is to this cause that Rinne refers some anomalous results obtained by Jaeger). The paper is accompanied by a magnificent series of exposures, including cyanite (anorthic); diopside, epidote, scolecite, and sucrose (monoclinic); anhydrite and aragonite (orthorhombic); calcite and dolomite (rhombohedral); quartz, carborundum, and beryl (hexagonal); cuprite and rock-salt (cubic)—as well as others illustrating typical "abnormalities." Rinne's elegant employment of the gnomonic projection is admirably illustrated by a basal exposure of anhydrite, which contains no fewer than 424 spots, contributed by as many planes belonging to 112 different crystal forms, most of which have never been observed as actual faces. The astonishing accuracy with which such complex crystal planes as (66.5.30), (88.45.40), (42.65.30) register their positions on the photographic film may be regarded as a most impressive demonstration of the orderly nature of crystal structure.

The molecular structure of a mixed crystal has been investigated by Vegard and Schjelderup[6] by means of the *X*-ray spectrometer. It is found that the reflection angles of mixed crystals of potassium chloride and potassium bromide vary regularly with the composition as deduced from Fock's solubility curves (the crystals were not chemically analysed). The mixed crystal, then, behaves as a single individual, and cannot be regarded as an intercalation of two independent lattices.

X-Ray spectra produced by curved crystal faces have been studied by Cermak.[7]

The chemical aspects of crystal-structure are being freely discussed. In the first place, it has been pointed out that Groth's denial of molecules is at least premature, if it is not clearly erroneous.[8] Further arguments for the existence of molecules are given by Smits and Scheffer,[9] who suggest valency models for rock-salt and calcite. Other chemists draw an analogy between co-ordination and crystal-structure; for example, Pfeiffer[10] points out

[6] L. Vegard and H. Schjelderup, *Physikal. Zeitsch.*, 1917, **18**, 93; *A.*, ii, 243.

[7] P. Cermak, *ibid.*, 1916, **17**, 405, 556.

[8] A. Fock, *Centr. Min.*, 1916, 392; A., ii, 129.

[9] A. Smits and F. E. C. Scheffer, *Proc. K. Akad. Wetensch. Amsterdam*, 1916, **19**, 432; *A.*, ii, 78.

[10] P. Pfeiffer, *Zeitsch. anorg. Chem.*, 1916, **97**, 161; *A.*, 1916, ii, 228; compare also P. Niggli, *ibid.*, 1916, **94**, 207; *A.*, 1916, ii, 300.

that rock-salt may be regarded as made up of $[NaCl_6]$ and $[ClNa_6]$. The chemical constitution of crystals is also discussed in Vegard's papers, but other practising *X*-ray analysts leave such questions severely alone. Chemists naturally look forward to the adoption of the idea of valency; crystal-physicists, on the other hand, have so far eschewed any appeal to valency, perhaps because the appeal would, from their point of view, imply another assumption. It is, however, possible that the appeal will ultimately have to be made in a case like sodium chlorate.

The appearance of theoretical papers by Niggli,[11,12] Johnsen,[13] Schönflies,[14] who discusses enantiomorphism, Beckenkamp,[15] and Rinne[16] may be put on record.

Fedorov's Critical Survey of the Work of W. H. and W. L. Bragg.

It must be remarked at the outset that the material used by Fedorov is restricted to the well-known book "*X*-Rays and Crystal Structure," a copy of which was sent out to him as soon as published. The main results of his analysis are presented in four papers.[17]

The first paper ("Results of the first stage of the experimental investigation of crystal-structure") is devoted to a critical survey of Bragg's results from the point of view of his own contributions to the theory of crystal-structure. Each crystal is studied in detail; the structural parallelohedron and point-system-symbol are determined; the various elements of symmetry (planes, glide-planes, axes, alternating axes, screw axes) are presented in the form of a structural diagram. In this way, rock-salt, ammonium chloride, cuprite, blende, diamond, fluorspar, calcite, dolomite, pyrites, zincite, and sodium chlorate are passed in review. Now the experimental investigation of these substances was not attended with equal success; for example, W. H. and W. L. Bragg regard their investigations of ammonium chloride, cuprite, zincite, and sodium chlorate as incomplete. These cases are examined at some length. It is pointed out that atoms generally occupy favoured positions in the structure; they are generally situated at points which are the intersections of several axes and planes of symmetry.

[11] P. Niggli, *Ber. K. Sächs. Ges. Wiss.*, [*Math.-Phys. Klasse*], 1915, **67**, 364.
[12] *Idem*, *Centr. Min.*, 1916, 497; 1917, 313.
[13] A. Johnsen, *ibid.*, 1916, 385.
[14] A. Schönflies, *Zeitsch. Kryst. Min.*, 1916, **55**, 321; *A.*, ii, 447.
[15] J. Beckenkamp, *Centr. Min.*, 1917, 97; *A.*, ii, 296.
[16] F. Rinne (two papers covering much the same ground), *Jahrb. Min.*, 1916, ii, 47; *Zeitsch. anorg. Chem.*, 1916, **96**, 317; *A.*, ii, 18, 166.
[17] E. S. Fedorov, *Bull. Acad. Sci. Petrograd*, 1916, **10**, 359, 435, 547, 1675.

and it might be concluded therefrom that the symmetry of an atom approximates to that of a sphere. This, however, cannot really be true, because it is incompatible with the property of valency, the operation of which must deform the atom; moreover, the zinc atoms in zincite must be polar if they are to account for the undoubted hemimorphism of structure. These considerations are held in view when Fedorov proceeds to suggest suitable structures for ammonium chloride, cuprite, and sodium chlorate. The optical activity of the last substance is fully discussed, and the author finds himself compelled to postulate asymmetry of the atom.

In the second paper (which contains some important corrections to the first) Fedorov enunciates "The fundamental law of chemical crystallography." Following is, perhaps, the most concise way of stating the law: The whole of the atoms of a crystal are situated at (some of) the nodes of a single, ultimate space-lattice. Various deductions can be made from the law. For example, it necessarily follows that a plane passing through any three atoms is a possible plane of development (face). Moreover, if we take an atom as origin, and three space-co-ordinates defined by the position of three other atoms of the same composition not lying in a plane with it, then the position of any other atoms can be stated in the form of co-ordinate numbers, which are small whole numbers or fractions. Thus, in the case of rock-salt, if the general co-ordinates of the sodium atoms are (000), the co-ordinates of the chlorine atoms are $(\frac{1}{2}00)$; for blende we have Zn$(\frac{1}{2}00)$ and S$(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$; for ammonium chloride, Cl(000), N$(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, H$(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$; for sodium chlorate, Na$(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$, Cl$(-\frac{1}{4}, \frac{1}{4}, \frac{1}{4},)$, O$(\frac{1}{4}00)$; for calcite, C(000), Ca$(\frac{1}{4}00)$, O$(\frac{1}{12}, -\frac{1}{12}\ 0)$, and so on. The author points out that as the law implies certain limitations on the possible positions of atoms, it can be employed in the deduction of the probable positions of atoms when the definite positions of others have once been settled by *X*-ray methods, and he is not afraid to amplify missing details in the structure of corundum and hæmatite (in which amplifications considerations of the centre of gravity of particular geometrical forms are relied on). Quartz and magnetite are also discussed with some detail. Suitable structures are also suggested for the following cubic substances: hexamethylenetetramine, tetramethylpyrazine, garnet, and potassium silicofluoride.

In the third paper ("The chemical side of crystal-structure"), Fedorov discusses briefly the connexion between atomic composition and atomic distances. The main conclusion (there are others) is that relative contiguity of two atoms is inversely related to the chemical degree of similarity; there is, however, a limitation with regard to bivalent atoms.

In the fourth paper ("A contribution to the problem of the determination of *atomic* reticular densities in crystal planes"), the author applies himself to a question, which is obviously of great crystallographic interest for the following reasons. Up to the present time, considerations of reticular density have suffered from two disabilities: (1) a total absence of intimate, experimental knowledge has always implied a purely theoretical treatment; (2) the theoretically possible point systems were relatively so complex that most crystallographers confined their practical attention to the much simpler space-lattice—in the hope that they may possibly ultimately advance from the simple to the complex; with the conviction that the opposite, alternative line of procedure would leave them permanently in the air. In spite of the above disabilities, the study of reticular densities has been both suggestive and fruitful. It has suggested a consistent way (that is, a way governed by a principle) of restricting the infinite number of axial ratios allowed by Haüy's law; it has been one of the factors (but not the only one) that has made it possible to apply crystal measurements to the identification of chemical substances. Fedorov recognises that it is now possible to study the subject of reticular densities with all exactness, and in the paper under review he discusses the problems opened up by atomic vistas. (It may be remarked, parenthetically, that somewhat similar problems were treated in a very interesting way many years ago by Sohncke).[18] Successive parallel strata frequently differ greatly in reticular density, and as he takes the view that the reticular density of the densest stratum carries most weight in the determination of the external form of the crystal, Fedorov determines these highest densities. As in previous work, the results are given in the form Δ^2, where Δ represents reticular density. All Bragg's cubic substances are studied.*

[18] L. Sohncke, *Zeitsch. Kryst. Min.*, 1887, **13**, 214.

* The above digest may be of some value, although the Reporter has not been able to devote much time to the papers. Published in a generally inaccessible language, without any French résumé, they are as good as lost to Western Science; an English translation is imperative before they can ever receive the attention they deserve. Professor Fedorov has published several other papers, but he has been unable to send separate copies owing to Russian postal regulations of a temporary character. Cross-references, however, indicate that some of these papers are devoted to a further development of crystallo-chemical analysis. As mentioned above, *X*-ray work entails much revision of some previous ideas. The Reporter has made an examination of the application of the Bravais principle (as employed before the advent of *X*-ray methods) to the new atomic re-constructions, and finds that the principle reveals the correct primary space-lattice (that is the three principal translation ratios of the whole structure) in every case elucidated by the *X*-ray analysts, but leads to erroneous conclusions in every possible

Stereochemical Reconstructions.

Since the appearance of the last Report, the following crystals have been fully elucidated.

Silver, Gold, and Lead.—In the case of silver,[19] the first-order reflection-angles agree closely with $d_{100}:d_{110}:d_{111}=1:1/\sqrt{2}:2\sqrt{3}$, ratios which are characteristic of the face-centred, cubic lattice, and a calculation of the number of atoms in the unit-cell confirms the deduction. The same structure was deduced for gold and lead,[20] the lead crystal having been obtained artificially by immersing zinc in a solution of lead acetate. In both cases, the investigation had to be restricted to the octahedral plane, owing to a platy habit. The structural deduction was based: (1) on the values of the glancing angles, and (2) on a normal distribution of intensity over the first three orders. These investigations prove that silver, gold, and lead have the structure previously deduced for copper by W. L. Bragg.

Anatase, TiO_2.—This polymorphous modification of rutile has been investigated by Vegard,[21] who finds the structure to be of Bragg's diamond type, but elongated along a fourfold axis to an extent implied by the ratio $c:a=1{\cdot}765$. Each titanium atom has two oxygen atoms (one above and one below) at distances equal to about one-fifth the vertical distance between successive titanium atoms.

Ammonium Iodide and Tetramethylammonium Iodide.—The X-ray investigations of these two substances we also owe to Vegard.[22] It is to be expected from its close crystallographic similarity that the first-mentioned compound should have precisely the same structure as rock-salt, and Vegard concludes that this is so, and that the nitrogen and iodine atoms interpenetrate, one set centring the cell faces of the other set.* The position of the

case (in the hexagonal and rhombohedral systems it cannot theoretically go wrong) with respect to the number and method of interpenetration of these primary lattices. Stated in other words, the principle reveals the correct axial ratios.

[19] L. Vegard, *Phil. Mag.*, 1916, [vi], **31**, 83; *A.*, 1916, ii, 186.

[20] *Idem, ibid.*, **32**, 65; *A.*, 1916, ii, 405.

[21] *Idem, ibid.*, **32**, 505; *A.*, 1916, ii, 593.

[22] *Idem, ibid.*, 1917, [vi], **33**, 395; *A.*, ii, 296.

* Vegard does not appear to have calculated the theoretical intensities demanded by his structure. Some values worked out by the Reporter for the octahedral reflections are given here:—

Order	1st	2nd	3rd	4th
Observed	100	90	20	20
Calculated	100	46	7	4·5

The discrepancies can scarcely be regarded with equanimity. It must

hydrogen atoms could not be fixed, owing to their relatively small mass. It is interesting to note that ammonium iodide is thereby proved to have a different structure from ammonium chloride, a conclusion which had been deduced previously by other methods. The structural dissection of the tetragonal tetramethyl derivative is, of course, a much more complicated problem. The dimensions of the elementary cell were found to be in accordance with *twice* the accepted axial ratio $c:a=0{\cdot}71$, but the natural expectation that the lattice should also have this double value led to no satisfactory reconstruction. In view of this, Vegard made the provisional assumption that the lattice has, indeed, the simple ratio $c:a=0{\cdot}71$, and eventually arrived at a reconstruction,* which cannot be described for lack of space.

Rutile Group.—This well-known isomorphous group of minerals, consisting of rutile, TiO_2 ($TiTiO_4$?), cassiterite, SnO_2 ($SnSnO_4$?), zircon, $ZrSiO_4$, and xenotime, YPO_4, has been subjected to a searching analysis by two independent workers, Vegard and Williams; the former examined the whole group; the latter confined his attention to rutile and cassiterite. In his first examination, Vegard[23] drew the conclusion that xenotime occupies a peculiar position structurally, but as a result of a later series of measurements,[24] with an improved form of spectrometer, he revises this conclusion. An apparently suitable structure for the whole group was offered by Vegard, but it appears from Williams'[25] work (which was just ready for publication at the time Vegard's paper appeared) that Vegard's reconstruction rests on the faulty basis that the 7°44′ (100)-reflection of rutile is a first-order reflection. This reflection was, indeed, also obtained by Williams, but it is preceded by a more intense reflection at an angle of 3°52′. Whilst the experimental data of the two workers agree quite well in other respects, it need scarcely be stated that the discovery of a "sub-first" order renders Vegard's reconstruction untenable. Following are the essentials of the structure suggested by Williams.

however, be observed that Vegard had to grind octahedral planes on his crystals. May the discrepancies be due to errors of grinding ?

* It must be pointed out that such a result is not merely surprising but exceedingly disconcerting. Unfortunately, it would seem to presage a certain want of trustworthiness in any dissection of crystal-structure which is not carried successfully to the utmost atomic limits. An extreme view to take would be that an *X*-ray dissection of crystal-structure must be completed before it has any value whatsoever. It is to be hoped that further work will serve to clear up this "irregularity."

[23] *Idem, ibid.*, 1916, [vi], **32**, 65, 505; *A.*, 1916, ii, 593.

[24] *Idem, ibid.*, 1917, [vi], **33**, 421; *A.*, ii, 296.

[25] C. M. Williams, *Proc. Roy. Soc.*, 1917, [A], **93**, 418; *A.*, ii, 450.

The fundamental tetragonal cell (Fig. 1), having the ratio $c:a=0{\cdot}644$, contains two molecules. There are two *simple* ways of fulfilling this condition: one is to centre the cell, the other to centre the basal plane. Neither of these two simple possibilities, however, is reconcilable with the experimental data. The structure finally offered is that given by Fig. 2 for the metallic atoms. [It can be regarded as made up of eight interpenetrating space-lattices, each having the proper translation-ratio $c:a=0{\cdot}644$.] A clue to the position of the oxygen atoms was obtained from the abnormal intensities of the second-order (001)-reflections, which point to an intercalation of oxygen atoms in these structural planes. The calculated and observed intensities agree very well. The original paper gives a picture of the complete structure, which exhibits tetragonal screw-axes and enjoys holohedral symmetry.

General Conclusions.—The work of W. H. and W. L. Bragg on calcite and sodium nitrate, as well as Vegard's work on zircon and

Fig. 1.

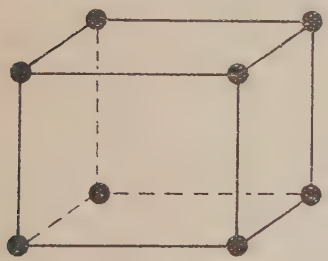
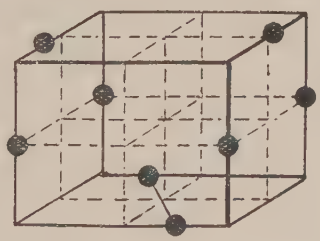


Fig. 2.



xenotime, brings to the forefront a question of the utmost chemical importance, namely, the chemical constitution of inorganic compounds. The work shows that the *stereochemical* formulæ of calcium carbonate and sodium nitrate on the one hand, and of zirconium silicate and yttrium phosphate on the other, are just as similar as, say, potassium sulphate and rubidium sulphate. Now the chemical similarity of the last pair is sanctioned by "constitutional" or "valency" formulæ, but this is not true of the first and second pairs. It need scarcely be pointed out that the constitutional formulæ of inorganic chemistry have been largely prompted by ideas derived from organic chemistry, and do not take sufficient account of ionic dissociation. A certain revision of inorganic formulæ is involved in the idea of co-ordination, and it appears likely that future developments of the theory of co-ordination will eventually restore consistency to "valency formulæ." (Are the "crystal formulæ" stereochemical or are they "stereophysical"?)

Topic-axes.

The fundamental correctness of the conception of topic-axes was involved in Bragg's demonstration that the reflection angles of the isomorphous potassium chloride and bromide have the simple relationship demanded by their respective molecular volumes. A paper by Tutton[26] is, however, none the less worthy of attention, since it deals with the more general cause of the orthorhombic system. It is shown that Ogg and Hopwood's[27] preliminary results prove conclusively that the absolute spacial distance of the molecular centres, in crystals of potassium, rubidium, cæsium, and ammonium sulphate, are indeed progressively increased to the extent precisely demanded by the molecular volumes, and that topic-axes are therefore a trustworthy measure of relative molecular distances in an isomorphous series. On the other hand, it is pointed out by Vegard[28] that topic-axes are liable to yield a considerable amount of misinformation in "morphotropic" as opposed to isomorphous comparisons. For example, the morphotropic regularities, supposed to exist by Groth, between ammonium iodide and tetramethylammonium iodide, have no real existence. This conclusion bears out a warning previously given by Barlow and Pope[29] that little, if any, value attaches to an indiscriminate calculation of topic-axes.

A. Ledoux[30] has published a paper on the question whether the topic-axes of isomorphous mixtures are a purely additive function of the composition—whether they are representable by straight graphs. The rhombic and monoclinic pyroxenes are selected as material, and the already existing data are supplemented by an extensive series of new measurements and density-determinations. In order to make the most rigid comparisons, it is necessary to "evaluate" the monoclinic angle β to 90°, and the author gives a mathematical solution of the problem. The general conclusion is that topic-axes are an additive function, except, of course, in cases of double-salt-formation.

The Valency Volume Theory.

A paper on the law of valency volumes has been published by Barlow,[31] who appears to take the view that the truth of the law

[26] A. E. H. Tutton, *Proc. Roy. Soc.*, 1917, [A], **93**, 72; *A.*, ii, 244.

[27] A. Ogg and F. L. Hopwood, *Phil. Mag.*, 1916, [vi], **32**, 518; *A.*, 1916, ii, 594.

[28] L. Vegard, *ibid.*, 1917, [vi], **33**, 419.

[29] W. Barlow and W. J. Pope, *ibid.*, 1915, [vi], **29**, 745; *A.*, 1915, ii, 427; compare also *Ann. Report*, 1915, 255.

[30] A. Ledoux, *Bull. Soc. franç. Min.*, 1916, **39**, 232; *A.*, i, 496.

[31] W. Barlow, *Min. Mag.*, 1916, **17**, 314; *A.*, 1916, ii, 228.

has been established by previous work, and that the law can accordingly be used as an instrument to probe the crystallographic relationships of allied substances. For example, in a series of comparisons between pairs of sulphates, it is shown that two out of the three spacial dimensions (given in the form of modified equivalence parameters) preserve a relatively constant ratio, whilst the third dimension varies as the total valency volume. This is held to lend support to an idea that strata of sulphate radicles and of metallic atoms pervade the crystal structure.

The theory has been commented on in two other papers. Ogg and Hopwood[27] have subjected the isomorphous potassium, rubidium, cæsium, and ammonium sulphates to a most thorough *X*-ray examination, and have obtained results which prove that the four salts are isotactic. The full working out of the intimate details has unavoidably been postponed, but the authors tentatively consider the structure is based on a face-centred lattice having the ordinarily accepted axial ratios $a:b:c=0{\cdot}5727:1:0{\cdot}7418$ (potassium salt). A brief examination is made of the bearings of their work on the valency volume theory. *X*-Ray data prove, for example, that the replacement of an atom of potassium by an atom of cæsium produces twice the distension brought about by the introduction of an ammonium group consisting of five atoms. This result is held to furnish conclusive evidence against the general truth of the theory. The difficulty of replacing one valency volume by seven, without extensive structural derangements, is developed by Tutton,[26] who points out, in a general discussion, that equivalence parameters obscure the crystallographic relationship between potassium, rubidium, and cæsium salts on the one hand and the ammonium salts on the other.

Some important Crystallographic Researches.

The monoclinic double selenates of the general formula

$$R_2Ni(SeO_4)_2,6H_2O,$$

in which R = K, Rb, Cs, and NH_4, have been subjected to a thorough morphological, volume, and optical investigation by Tutton.[32] The results confirm all previous conclusions obtained in former studies of this well-known group of double sulphates and selenates. It is also pointed out that the crystallographic regularities of potassium, rubidium, and cæsium salts may be referred to a regular sequence of atomic numbers in lieu of atomic weights.

The great value of a crystallographic investigation in doubtful cases of isomerism is demonstrated by a recent paper by Bennett.[33]

[32] A. E. H. Tutton, *Phil. Trans.*, 1917, [A], **217**, 199; *A.*, ii, 415.

[33] G. M. Bennett, *T.*, 1917, **111**, 490; *A.*, i, 449.

It is shown that the α- and β-forms of sodium ferrocyanide are really crystallographically identical. This, of course, rules out any possibility of isomerism. The same is true for the reputed isomerism of potassium ferrocyanide.

A more frequent use of the polarising microscope in chemical investigations is advocated by Wright,[34] who has done much to improve microscopic methods.[35] The maximum and minimum refractive indices of a crystal can be rapidly determined to the second (perhaps the third) decimal place. The identification of sugar-osazones and alkaloids is illustrated by numerous examples. The author, however, does not seem to be aware of the existence of immense tables (built up on similar lines) by Kley[36] and Bolland[37]—the Reporter came across them accidentally.

Karandéev[38] has added still another example to the list of biaxial crystals of proved rotatory power. The new example is quercitol, $C_6H_7(OH)_5$, originally measured by Lewis. The author accepts Lewis' axial ratios and amplifies the description by the determination of the correct setting and complex-symbol. The optic axes lie in the plane of symmetry, and consequently may have different rotatory powers. This theoretical possibility is experimentally realised; for 1 cm. thickness the respective rotations for, say, sodium light are $-35°$ and $-46°$. It is also interesting to note that a solution is dextrorotatory. The whole investigation is an excellent example of the efficiency of the most recent goniometrical and optical methods.

An interesting case of racemism and pseudo-racemism has been investigated by Miss Kaplanova.[39] The active modifications of the hydrochloride, hydrobromide, and hydriodide of glutamic acid are isomorphous with the *dl*-forms of the hydrochloride and hydrobromide, but the *dl*-form of the hydriodide crystallises in another system, and is therefore a true racemate.

V. Rosický[40] has courageously attempted to unite crystal densities and refractive indices in a novel way with a view to compare the values of the new constants in isomorphous series.

A new case of tetramorphism is announced,[41] namely, that of 2:6-dinitro-*p*-toluidine.

[34] F. E. Wright, *J. Amer. Chem. Soc.*, 1916, **38**, 1647; *A.*, 1916, ii, 571.
[35] F. E. Wright, *J. Washington Acad. Sci.*, 1916, **6**, 465.
[36] P. D. C. Kley, *Rec. trav. chim.*, 1903, **22**, 367; *A.*, 1904, ii, 99.
[37] A. Bolland, *Sitzungsber. K. Akad. Wiss. Wien* [Abt. II. b. (Chemie), 1908, **107**, 671; 1910, **119**, 275, 1191.
[38] V. V. Karandéev, *Bull. Acad. Sci. Petrograd*, 1915, **9**, 1285.
[39] L. Kaplanova, *Abh. Böhm. Akad.*, 1915, No. 23; *A.*, i, 547.
[40] V. Rosický, *Rozpravy české Akad. Prag*, 1911, **20**, No. 5; *A.*, ii, 433
[41] E. Artini, *Atti R. Accad. Lincei*, 1917, [v], **26**, i, 392; *A.*, i, 389.

Eutectic structures in binary mixtures of organic compounds (varying proportions of camphor and benzoic acid, *p*-nitroaniline, *p*-dibromobenzene, phthalic anhydride, naphthalene, acetamide, salicylic acid, methyl thiocyanate) have been studied by Efremov.[42] There are numerous excellent plates.

An interesting example of eutectic structure is that known to mineralogists as "graphic granite." This complicated phenomenon is being investigated by Fersman,[43] who has succeeded in deducing a law which governs the relative orientation of felspar and quartz; the prismatic zone of felspar is parallel to the rhombohedral edge of quartz. It is shown that all previous observations fit in with this law. The author is preparing a monograph on this interesting subject. Graphic granite is probably not a eutectic.[44]

The linear force of growing crystals is discussed in a paper by Becker and Day.[45] It is shown that a growing crystal has the power of raising a superimposed weight, provided no other crystals (free from weights) are present in the solution. This interesting observation receives a satisfactory theoretical explanation; the effect of a load is to increase the solubility of the individual crystal.

Anisotropic Liquids ("Liquid Crystals").

A considerable body of literature on anisotropic liquids is to be noted. In the first place, a long series of papers has been published by O. Lehmann,[46] who is evidently nursing quite a collection of grievances and is distressed to find that some of his views have been annexed by others without a suitable acknowledgment. It is a pity that the Karlsruhe physicist cannot bring himself to write out a calm statement having a low coefficient of irritation, for some of us wish to read him. It would also be a help if new observations were rigorously segregated. On the other hand, a judicious estimate of our present knowledge of "liquid crystals" has been given by Voigt,[47] and the value of his contributions are enhanced by a mathematical treatment; but it is to French observers that we owe the most interesting developments. The notable experiments of C. Mauguin (who at present "is gloriously carrying out his duties in the trenches which defend the approaches

[42] N. N. Efremov, *Bull. Acad. Sci. Petrograd*, 1915, **9**, 1309.
[43] A. E. Fersman, *ibid.*, 1211.
[44] J. de Lapparent, *Bull. Soc. franç. Min.*, 1917, **40**, 111.
[45] G. F. Becker and A. L. Day, *J. Geol.*, 1916, **24**, 313.
[46] O. Lehmann, *Ann. Physik*, 1915, [iv], **46**, 832; **48**, 177, 725; 1916, **51**, 353; 1917, **52**, 445, 527, 541.
[47] W. Voigt, *Physikal. Zeitsch.*, 1916, **17**, 76, 128, 152, 305.

to Nancy")[48] were described in the 1914 Report. As early as 1913, Mauguin[49] made the observation that "liquid crystals" of azoxyanisole take up a definite orientation on a cleavage surface of mica (muscovite); a similar observation was independently made by "Captain-of-Artillery" Grandjean,[50] who extended the observations, and has recently brought them to the publication stage. The experimental material consisted of ten organic substances and the following minerals: orpiment, blende, phlogopite, brucite, talc, pyrophyllite, muscovite, rock-salt, sylvine, and leadhillite. Fresh cleavages must be used. Regular orientations were obtained in ninety cases out of the possible hundred; in some cases the orientation is independent of the temperature; in other cases it changes either discontinuously or continuously with the temperature. The continuous variation proves that the property is not necessarily due to an alignment of the molecular axes of the liquid on a row of structural particles in the crystal-lattice, but is an equilibrium property of a more general, capillary nature The author believes that the observations point to (what the Reporter reads to be) action at a distance.

Mineralogical Chemistry.

A valuable paper on "secondary enrichment" deserves the general attention of mineralogists. It is well known that the surface oxidation of copper ores gives rise to copper and iron sulphates; the latter is rapidly hydrolysed to hydroxide, and the liberated sulphuric acid and copper sulphate percolate through the unoxidised ore and cause a secondary enrichment. The problems of secondary enrichment are of great chemical interest and of considerable economic importance, and are being extensively studied in America from all points of view. A recent paper by Zies, Allen, and Merwin[51] throws much light on the chemical changes involved. The action of acidified solutions of copper sulphate on redruthite, Cu_2S, covellite, CuS, erubescite, Cu_5FeS_4,[52] chalcopyrite, $CuFeS_2$, pyrrhotite, $FeS + nS$, pyrites, FeS_2, blende, ZnS, and galena, PbS—was investigated at temperatures up to 200° with a proper equipment of autoclaves.[53] In most cases, the real (as

[48] Presidential Address, *Bull. Soc. franç. Min.*, 1915, **38**, 5.

[49] C. Mauguin, *Compt. rend.*, 1913, **156**, 1246.

[50] F. Grandjean, *Bull. Soc. franç. Min.*, 1916, **39**, 164; *A.*, ii, 451; *ibid.*, 1917, **40**, 69.

[51] E. G. Zies, E. T. Allen, and H. E. Merwin, *Economic Geology*, 1916, **11**, 407; *A.*, ii, 91.

[52] E. T. Allen, *Amer. J. Sci.*, 1916, [iv], **41**, 409; *A.*, 1916, ii, 391.

[53] G. W. Morey, *J. Washington Acad. Sci.*, 1917, **7**, 205; *A.*, ii, 305.

opposed to "descriptive") chemical equations have been determined. Thus the alteration of pyrites to redruthite is strictly according to the equation:

$$5FeS_2 + 14CuSO_4 + 12H_2O = 7Cu_2S + 5FeSO_4 + 12H_2SO_4.$$

The general effect of copper sulphate solution is expressed as follows: chalcopyrite $\longrightarrow$ covellite $\longrightarrow$ redruthite, which is very stable at the ordinary temperature, and even at 200° is only transformed very slowly into copper and sulphuric acid. Secondary reactions begin to play an important rôle at high temperatures; thus cupric and ferrous sulphates are partly transformed into cuprous and ferric sulphates, and subsequent hydrolysis may give hæmatite, Fe_2O_3, cuprite, Cu_2O, and metallic copper. Cuprous sulphate is more reactive than cupric sulphate. The general effect of free sulphuric acid is to retard the formation of cuprous sulphate.

The much vexed question of the various forms of calcium carbonate has, perhaps, received a final solution at the hands of Johnston, Merwin, and Williamson.[54] These authors conclude from a critical survey of previous investigations, supplemented when necessary by new observations, that the only real forms are calcite, aragonite, and a new form, μ-calcite, which is not very stable in presence of water. Further, there is a definite hexahydrate. Four reputed forms are considered to be superfluous: vaterite is a porous calcite, conchite and ktypeite are porous aragonites, whilst lublinite has been definitely proved by Quercigh[55] to be a "variety" of calcite. Under ordinary pressure, calcite is the stable form at all temperatures. Aragonite changes pseudomorphously into calcite at rates which increase with the temperature, the change being almost instantaneous at 470°; it also changes more or less rapidly in presence of water—at 100°, two weeks are necessary. There is, however, indirect evidence for a reversible transformation at $-100°$ (private communication of R. C. Wells). The preparation of μ-calcite is not a suitable lecture experiment. It is best obtained at 60°, and is always contaminated with calcite and aragonite; D = 2·54 or higher; $\mu_1 = 1·55$, $\mu_2 = 1·65$. System, hexagonal. The hexahydrate is monoclinic; $2E = 72° \pm 3°$; $\alpha = 1·460$, $\beta = 1·535$, $\gamma = 1·545$.

The rôle of inorganic agencies in the deposition of calcium carbonate has been discussed by Johnston and Williamson.[56]

[54] J. Johnston, H. E. Merwin, and E. D. Williamson, *Amer. J. Sci.*, 1916, [iv], **41**, 473; *A.*, 1916, ii, 433.

[55] E. Quercigh, *Rivista Min. Crist. Ital.*, 1916, **44**, 65.

[56] J. Johnston and E. D. Williamson, *J. Geol.*, 1916, **24**, 729; *A.*, ii, 213.

W. F. Hallimond[57] has published a study of the crystallography and dehydration of the complex copper uranyl phosphate, torbernite, $Cu(UO_2)_2(PO_4)_2,8H_2O$. The most probable axial ratio is $c:a=2{\cdot}974$; there is no weighty crystallographic evidence against the system being tetragonal. The *pt*-dehydration curve of torbernite $\longrightarrow$ meta-torbernite I (the change is irreversible) was mapped out in an ingenious manner. The author has observed that loss of water is confined to the edges or pyramidal faces of the crystals, and he makes the interesting suggestion that loss of water through the basal plane is prevented by the high reticular density in this plane, demanded alike by perfect cleavage and the high value $c:a$.

Mention must be made of a "paper" of 1200 pages by Washington,[58] in which all igneous-rock analyses published in the period 1884—1913 are critically discussed.

Thermal Studies of Mineral Systems.

As mentioned in the introduction, the thermal studies of mineral systems, undertaken especially by American workers, are already leading to important practical conclusions. It must be noted that attention is no longer confined to anhydrous systems. A most comprehensive investigation of the system *water–potassium metasilicate–silica* has been undertaken by Morey.[59] The Reporter must state quite frankly that he has not yet succeeded in reducing the results of this investigation to a moderate compass; so, for the present, he asks leave to proceed to some anhydrous systems.

Binary System, Soda-nepheline–Potash-nepheline, $(Na,K)AlSiO_4$.—For the essential details of this system, consult the abstract.[60]

System, Iron–Oxygen.—The portion of this system which relates to the important minerals hæmatite, Fe_2O_3, and magnetite, Fe_3O_4, has been subjected to a remarkable experimental study by Sosman and Hostetter,[61] who have determined the pressures of oxygen (due to dissociation) in a specially constructed vacuum-furnace. A series of measurements was carried out at 1100° and 1200°. The dissociation pressures are quite small; thus at 1100° the pressure is 0·37 mm. over hæmatite and $<0{\cdot}005$ over magnetite. The change $3Fe_2O_3 \rightleftarrows O+2Fe_3O_4$ is proved to be reversible, for

[57] W. F. Hallimond, *Min. Mag.*, 1916, **17**, 326; *A.*, 1916, ii, 258.

[58] H. S. Washington, *U.S. Geol. Survey*, 1916, Professional Paper 99.

[59] G. W. Morey and C. N. Fenner, *J. Amer. Chem. Soc.*, 1917, **39**, 1173; *A.*, ii, 370.

[60] N. L. Bowen, *Amer. J. Sci.*, 1917, [iv], **43**, 115; *A.*, ii, 178.

[61] R. B. Sosman and J. C. Hostetter, *J. Amer. Chem. Soc.*, 1916, **38**, 807; *A.*, 1916, ii, 331.

identical oxygen pressures are obtained indifferently by oxidation of magnetite or by dissociation of pure ferric oxide. The two oxides form a continuous series of solid solutions. Further work by the same authors[62] shows that ferric oxide exhibits a small but measurable dissociation when heated in air at 1100—1300°, and that the amount of dissociation increases with the temperature. Again, the equilibrium relationships of hæmatite and magnetite have been probed[63] by a determination of the magnetic susceptibility of a carefully analysed series of natural and artificial products. This susceptibility is proved to be approximately proportional to the ferrous oxide content. Finally,[64] the interesting observation was made that certain crystals of hæmatite from Elba exhibit a zonal structure, in which magnetic susceptibility goes hand in hand with the amount of ferrous oxide in the various zones; the authors' researches indicate that such variations can be readily interpreted as due to fluctuations of temperature and pressure during crystal growth.

Ternary System, CaO–Al_2O_3–MgO.[65]—Consult abstract.

Ternary System, Diopside–Albite–Anorthite.[66]—Bowen's experimental study of the equilibrium relationships of these three components derives great importance from its high petrological significance; although it is true that pure substances were advisedly employed (whereby the system becomes less complicated than the average natural rock system), yet the results obtained can safely be held to present the main features of the natural history of basalts and diorites, and, with proper prudence, may even be applied to the elucidation of more remote problems. Of the three binary systems concerned, the plagioclase series of solid solutions (albite–anorthite) has been described in a previous Report.[67] Diopside and anorthite present an ordinary eutectic at 1270° (42 per cent. anorthite); finally, the position of the eutectic diopside–albite (about 97 per cent. albite) could only be obtained by extrapolation, owing to the sluggishness of crystallisation of albite fusions. The ternary system was explored by the quenching method,[68] and, as is only to be expected from the existence of continuous solid solutions of plagioclase, does not present any absolute ternary

[62] J. C. Hostetter and R. B. Sosman, *J. Amer. Chem. Soc.*, 1916, **38**, 118; *A.*, 1916, ii, 440.

[63] R. B. Sosman and J. C. Hostetter, *Bull. Amer. Inst. Min. Engineers*, 1917, 907.

[64] *Idem, ibid.*, 933.

[65] G. A. Rankin and H. E. Merwin, *J. Amer. Chem. Soc.*, 1916, **38**, 568; *A.*, 1916, ii, 249.

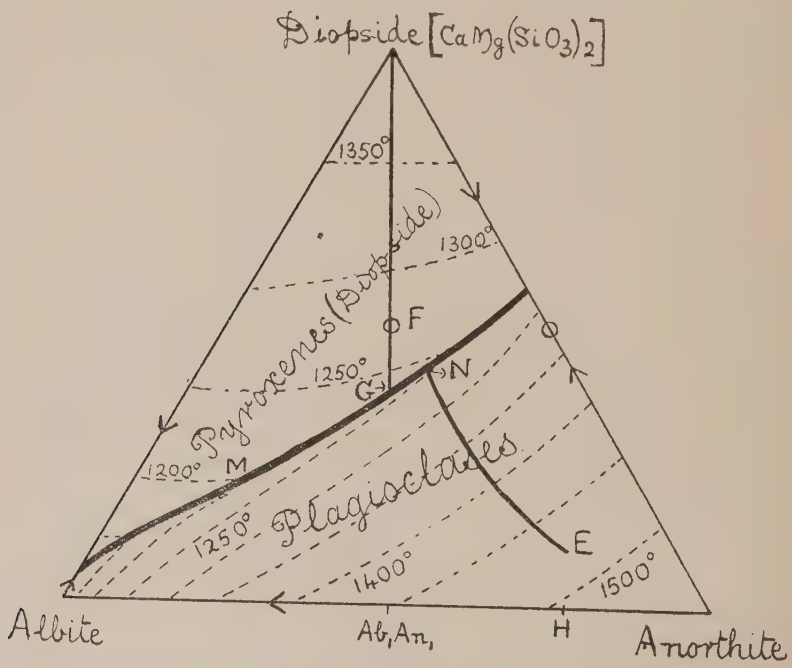
[66] N. L. Bowen, *Amer. J. Sci.*, 1915, [iv], **40**, 161; *A.*, 1915, ii, 694.

[67] *Ann. Report*, 1913, 254.

[68] *Ibid.*, 1914, 253

eutectic. This disposes of a whole mythology of neolithic antiquity. The results are conveniently embodied in the usual equilateral diagram (Fig. 3), reference to which will facilitate a discussion of the course of crystallisation of two typical mixtures. The composition of the first mixture (50 per cent. diopside, 25 per cent. albite, 25 per cent. anorthite) is represented by the point *F*. The dotted isotherms indicate that crystallisation begins at 1275°, and, as pure diopside separates, the composition of the residual fusion moves along the line *FG* until the boundary curve diop-

FIG. 3



side–plagioclase is reached. Further cooling is now signalised by the appearance of plagioclase (and, of course, more diopside), the composition of the plagioclase, as determined experimentally, being Ab_1An_4 (the point *H* of the diagram). Any subsequent cooling leads to a simultaneous separation of diopside and a series of plagioclases—richer and richer in albite; contemporaneously, previous generations of plagioclase crystals, if sufficiently minute, will dissolve progressively, but, on the other hand, they may be protected by a zonal coating of material having an equilibrium-composition, and in that way survive. Under ordinary conditions (that is,

when protected by zoning), the final composition of the last trace of liquid lies at some point on the boundary curve beyond M, but under ideal conditions the last solidification would be at M.

The second type of mixture is that in which plagioclase is the first to crystallise. A mixture, E (10 per cent. diopside, 90 per cent. $Ab_{18}An_{82}$), begins to crystallise at 1480°, with the separation of Ab_5An_{95}, and the composition of the liquid follows the curve EN. The path of such curve is no light matter to determine, but an ingenious combination of isotherms and "isofracts" (curves of equal refractive index; note: refractive index determines the chemical composition of a mixture) was found to suffice. At the point N (1245°) diopside begins to appear, and the subsequent course of crystallisation is similar in principle to that described above.

Relying on the above investigation and on similar researches of precision, already noted in these Reports, Bowen[69] proceeds to a masterly discussion of the problem of the origin of igneous rocks in general. He shows that there is no necessity to postulate either the existence of a number of magmas or the differentiation of an original magma into two or more immiscible fluids prior to crystallisation. On the contrary: an originally basic magma will, on cooling, give rise to a series of minerals ranging from ultra-basic to ultra-acidic; moreover, a sinking of relatively heavy crystals supplies just that sorting-out process which is needed for the formation of rocks of such different types as peridotites, basalts, diorites, granites, and syenites. Bowen's arguments are punctuated by a wealth of field evidence, chiefly collected by American geologists. In a later paper,[70] he examines the question as to the origin of mono-mineralic rocks, especially the anorthosites, which have been observed in immense masses in the Adirondacks and in the Morin District of Canada. Two truths are pretty obvious from the diagram (Fig. 3): (1) a copious crystallisation of plagioclase can only occur after a large proportion of pyroxene has separated, and, presumably, sunk by virtue of its high density; (2) when plagioclase crystals have separated in quantity, there is but little residual liquid, and it would seem that the magma should now be too viscous to penetrate surrounding rocks in the form of dykes. Field evidence does, in fact, demonstrate the absence of intrusive outliers from the main mass, and also that the adjoining syenites are due to a later stage of crystallisation.

[69] N. L. Bowen, "The later stages of the evolution of igneous rocks"—issued as a supplement, and bound with, *J. Geol.*, 1915, **23**.

[70] N. L. Bowen, *ibid.*, 1917, **25**, 209.

Crystal Growth and Dissolution.

Stability of the Plane Surface on a Growing Crystal.

General observation of crystal forms warrants the conclusion that a plane-faced polyhedron represents the natural boundary of a growing crystal. The conclusion derives support from numerous experiments. It was early observed that when an artificially fractured crystal is placed in a supersaturated solution, it grows more quickly at the fractured part, and the common statement is that it gradually takes up its original form. Most diverse observations on this point are recorded by Rauber,[71] who was so struck with the inherent powers of a "mutilated" crystal to heal itself that he was led to propound the theory that crystals are controlled by vital forces. Rauber's studies were purely qualitative. Later investigations in this interesting province we owe to Arteméev,[72] who by the help of the two-circle goniometer checked the "healing" process with exact measurements. The method adopted was to grind a crystal hemisphere of 5 or 10 mm. diameter and cement it to a corresponding glass hemisphere. The composite sphere was then suspended in a slightly supersaturated solution, taken out from time to time, and examined on the goniometer. The systems studied were cubic, monoclinic, and anorthic. The general behaviour is as follows. In the first period of growth, the sphere exhibits a number of glittering spots (on the goniometer) corresponding with the most important faces. The rest of the surface remains matt, but later becomes covered with tiny crystals in parallel position, each of which contributes a part to sharp goniometer reflections of the important forms; simultaneously, reflections corresponding with less important forms appear as glimmering points. As growth proceeds, the less important faces disappear, the tiny, parallel crystals coalesce, and the final result is a hemicrystal wholly bounded by common faces. Arteméev's method is likely to receive considerable attention on account of the valuable light it throws on other problems. Thus, inasmuch as the transitory faces often include general forms $\{hkl\}$, the class of symmetry may be elucidated; for example, in the case of alum, the form $\{210\}$ is hemihedrally developed as the pentagonal dodecahedron. Again, the method might be employed with advantage whenever the natural crystal fails to develop those facets which are necessary for a full calculation of the axial ratios.

[71] A. Rauber, "Die Regeneration der Krystalle," 1895-1896.

[72] D. N. Arteméev, *Zeitsch. Kryst. Min.*, 1910, **48**, 417; *A.*, 1911, ii, 24.

The Curved Surfaces of a Dissolving Crystal.

Experimental attention to this question appears historically to have passed through three well-defined phases, namely: (1) etching studies of crystal-faces; (2) observations of the successive forms assumed by a sphere when subjected to an all-round action of a dissolvant; and (3) investigations of the alteration of form brought about by a reversal of the growth process owing to the action of slightly unsaturated solutions. Observations belonging to the first and second class are largely coupled with the use of "chemical dissolvants." In recent years, we owe much to the work of V. Goldschmidt[73] and his co-workers. Thus, extensive investigations have been made on the etching of both natural crystals and spheres of calcite by means of phosphoric, hydrochloric, nitric, formic, and acetic acids. The sphere is first etched in tracts corresponding with those natural faces which are especially prone to attack, namely, $c\{111\}$, $r\{100\}$, and $f\{\bar{1}11\}$. A total disappearance of the etch-figures marks the next stage; the entire surface becomes affected, the *poles* of the above-mentioned faces becoming most sharply pronounced *corners* of curved faces. This emphasises the inverted relationship of growth and dissolution. As solution goes on, these inversion-corners shift slightly (but their movements are in accordance with crystal-symmetry) until at last a "final form" is reached which dissolves without change of shape. The final form appears to depend, first, on the original form of a natural crystal (not, of course, if a sphere has been ground), and, secondly, on the acid used and its concentration. In any case, it is wholly bounded by curved faces. Similar results were obtained with zinc blende.[74] The above investigations have thrown much light on the manifold corrosion forms exhibited by natural crystals of the diamond.[75]

Results in substantial agreement with the above have been obtained by Schnorr[76] in his study of the dissolvant action of slightly unsaturated solutions of sodium chloride (containing carbamide) on crystals of rock-salt. The first action is to bevel the cube edges with the form $\{hk0\}$; the value h/k changes progressively. The cube-corners are then modified by faces of the icositetrahedron $\{hkk\}$, which reduce and finally extinguish the $\{hk0\}$ forms; the value h/k depends on the degree of unsaturation

[73] V. Goldschmidt and F. E. Wright, *Jahrb. Min. Beil.-Bd.*, 1903, **17**, 355; **18**, 335. The first paper contains a copious bibliography of earlier work, including ordinary etch-figures. [74] P. Hochschild, *ibid.*, 1908, **26**, 178.

[75] A. E. Fersman and V. Goldschmidt, "Der Diamant," 1911.

[76] W. Schnorr, *Zeitsch. Kryst. Min.*, 1915, **54**, 289; *A.*, ii, 469.

of the solution, but in any case $\{hkk\}$ represents the final form. The behaviour of a sphere is very instructive. Etch-hollows first appear on the octahedron-poles; then corners of the icositetrahedron appear at the cube-poles, the final form being the icositetrahedron. Numerous experiments with solutions containing different amounts of carbamide proved that the final form obeys Goldschmidt and Wright's "law of polarity"; the corners of a dissolving crystal correspond with the face-poles of a growing crystal.

Curie's Capillarity Theory.

Acording to Curie's theory,[77] the most stable form which can be assumed by a crystal as a result of capillary forces is that for which the total surface energy is a minimum. Each crystal face has its specific capillarity constant, measured by the work involved in increasing the extent of the face by the unit of area. If we denote the areas of the various faces by S_1, S_2, S_3, . . ., and the capillarity constants by A_1, A_2, A_3, . . ., then the stable form of the crystal will be that for which $\Sigma(A_1S_1+A_2S_2+A_3S_3 \ldots)$ is a minimum for a given volume. It will be clear that a knowledge of these capillarity constants would enable us to predict the form of a crystal; for example, in the case of a cubic crystal like common salt, in which the cube and octahedron faces are frequently observed, the crystal could alternatively only develop cube or octahedron faces accordingly as $A_{100}:A_{111}<1/\sqrt{3}$ or $>\sqrt{3}$. An attempt was made to determine the constants for common salt by measuring the angle that the edge of a drop makes with the face on which it lies,[78] such angle being supposed to be related to the capillarity constant by a formula given by Gauss. Although the values fluctuated considerably for different specimens, they appeared to demonstrate the existence of capillarity differences; moreover, the relative values cube:octahedron were reversed by addition of a sufficient amount of carbamide, the presence of which is well known to favour an octahedral development. These results, however, were unfavourably criticised by Pockels.[79]

Curie's theory acquired considerable notice from its inclusion in Ostwald's "Lehrbuch." The theory demands that large crystals must grow at the expense of small ones in favourable circumstances, as, for example, when the temperature is fluctuating slightly. The question whether small crystals are the more readily soluble was investigated by Hulett,[80] who determined the sparing solubilities

[77] P. Curie, *Bull. Soc. franç. Min.*, 1885, **8**, 145.
[78] S. Berent, *Zeitsch. Kryst. Min.*, 1896, **26**, 529.
[79] F. Pockels, *Naturwiss. Rundschau*, 1899, **14**, 383.
[80] G. A. Hulett, *Zeitsch. physikal. Chem.*, 1901, **37**, 385; *A.*, 1901, ii, 493.

involved in the cases of gypsum and barium sulphate in terms of electric conductivity. For the former substance, he was able to demonstrate a temporary exhaltation; particles having approximately a radius of 0·0003 mm. gave a solubility of 18·2 millimols. per litre, whilst particles with a radius of 0·002 mm. gave the normal solubility of 15·33 millimols. Similar results were obtained with barium sulphate. It is important to note how small must be the crystal particles in order to obtain differences of solubility, owing to surface tension.

Relative Velocities of Growth.

Crystallographically, Curie's theory first acquired something more than academic interest when Wulff[81] published an important research on the relative velocities of growth of crystal-faces, that is, the relative rates at which each face advances from the centre of the crystal. The substance selected was Mohr's salt,

$$(NH_4)_2Fe(SO_4)_2,6H_2O$$

(monoclinic), and the following rates of growth were determined: $(\bar{2}01)=1{\cdot}00$, $(110)=1{\cdot}96$, $(001)=2{\cdot}25$, $(111)=2{\cdot}50$, $(\bar{1}11)=2{\cdot}64$, $(011)=2{\cdot}77$. Accepting Curie's theory, Wulff essayed to go a step further by offering a proof that these relative velocities of growth, which can be easily determined, are, in fact, proportional to the capillarity constants. It was, however, pointed out by Hilton[82] that the method of proof was faulty; a rigorous proof was advanced. Another proof has been given recently.[83] Now, Wulff adopted the view that the truth of the theory was established by his work; but Friedel[84] has recently pointed out that Wulff obtained the same results with crystals of different habits, and this shows that a distorted crystal does not tend to approach an ideal form. Fastert's[85] observations on the growth of common salt point the same way.

Relative Velocities of Dissolution.

Experimental determinations of rates of solution can, from the nature of the case, never be exact. The faces become pitted; the edges round off; the crystal altogether fails to preserve the clean-cut edges and plane faces characteristic of steady growth. Wulff

[81] G. Wulff, *Zeitsch. Kryst. Min.*, 1901, **34**, 385. The work appeared in Russian in 1895.

[82] H. Hilton, *Centr. Min.*, 1901, 573. Also consult his "Mathematical Crystallography," 1903, 105.

[83] H. Liebmann, *Zeitsch. Kryst. Min.*, 1914, **53**, 171.

[84] G. Friedel, *J. Chim. phys.*, 1913, **11**, 478; *A.*, 1913, ii, 844.

[85] C. Fastert, *Jahrb. Min., Beil.-Bd.*, 1912, **33**, 265.

found that all faces of Mohr's salt dissolve at the same rate. Körbs,[86] however, found different rates for a few substances (especially potassium ferrocyanide) out of a much larger number investigated.

Have Crystal Faces Different Solubilities?

The assumption that different faces have different solubilities is really involved in Curie's theory, for without the assumption it is impossible to conceive how a distorted crystal can assume the true equilibrium form (with minimum surface energy) when suspended in a saturated solution unless certain faces dissolve whilst others grow. The earlier attempts to settle the question were indirect and have led to nothing but controversies. Le Blanc[87] was the first to point out that the only satisfactory way of deciding the question is to see whether it is possible to realise such a concentration of solution that one face of a crystal grows whilst another dissolves. Experiments on the "prism" (which prism?) and cleavage pinacoid of potassium dichromate were cautiously held to be inconclusive. A notable research by Valeton[88] appears to be decisive. A solution was made to circulate through two vessels (held in separate thermostats), one containing the crystal under examination, the other containing a supply of solid solute. The relative temperatures of the two vessels could then be varied ever so slightly, so as to cause growth or dissolution at will. Growth or dissolution was detected by examining the crystal on the goniometer; a growing crystal gives sharp reflections, a dissolving crystal a band of reflections. The thermostats could be held constant to 0·001°. An increment in the temperature difference of the two vessels amounting to 0·003° was sufficient to transform unmistakable growth into unmistakable dissolution. A long series of experiments proved that it was not possible to obtain conditions at which cube or dodecahedron faces of alum dissolve whilst octahedron faces grow. The crystals investigated varied between 2 and 20 mm. in diameter.

[86] A. Körbs, *Zeitsch. Kryst. Min.*, 1907, **43**, 433.

[87] M. Le Blanc and G. Elissafov, *Ber. K. Sächs. Ges. Wiss.*, [*Math.-Phys. Klasse*], 1913, **65**, 199; *A.*, 1914, ii, 268.

M. Le Blanc and I. I. Andréev, *Zeitsch. physikal. Chem.*, 1911, **77**, 635.

[88] J. J. P. Valeton, *Ber. K. Sächs. Ges. Wiss.*, [*Math.-Phys. Klasse*], 1915, **67**, 1.

Thermodynamic Deductions.

In his work, "On the equilibrium of heterogeneous substances," and some years before Curie published his theory, Gibbs[89] deduced that $\Sigma(A_1S_1+A_2S_2+\ldots)$ has a minimum value for constant volume; but he went further, and made the deduction that the *tendency of a crystal to take up the equilibrium form is inversely proportional to its linear dimensions.* In an interesting discussion on crystal growth, he adds: "On the whole, it seems not improbable that the form of very minute crystals in equilibrium with solvents is principally determined by the condition that $\Sigma(A_1S_1+\ldots)$ shall be a minimum for the volume of the crystal, but as they grow (in a solvent no more supersaturated than is necessary to make them grow at all), the deposition of new matter on the different surfaces will be determined more by the nature (orientation) of the surfaces and less by their size and relations to the surrounding surfaces."

The connexion between capillarity constants and solubilities has been discussed by Berthoud.[90] Thermodynamic conditions of equilibrium are studied by Valeton and by Friedel. The latter concludes that "Curie's theory is applicable to liquid crystals, if such crystals exist."

T. V. Barker.

[89] J. W. Gibbs, "Scientific Papers," 1906, **1**, 320–326.
[90] A. Berthoud, *J. Chim. phys.*, 1912, **10**, 624; *A.*, 1913, ii, 305.

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